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THE FOLLOWING PAGES ARE CHANGES

TO BASIC DOCUMENT

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To all Holders of NOLTR 61-138
insert change; write on cover 'Change 2 inserted'
Approved by Commander, U.S. NOL

Change 2
16 November 1964
21 pages

ALBERT LIGHTBODY
By direction

This publication is changed as follows:

1. Page 69, delete all material under PROPELLANTS and all material down to PROCESS REVIEW on page 70.
2. Insert pages 69a thru 69t - inclusive attached herewith.

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Insert this change sheet between the cover and the title page of your copy.

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PROPELLANTS
INTRODUCTION

Solid propellants, like pyrotechnics, to be effective must release substantial quantities of energy as heat plus large volumes of gases. The energy of propellants is released during longer periods of time than the energy of explosives. In spite of this slower energy release from propellants it is fast enough so that in case of accident the resulting destruction may appear to be equal to that of an explosion. After viewing an accident involving propellants, it is often very difficult to believe that an explosion did not occur, and in fact, explosions do occur.

The hazards of propellant processing are usually greater than the hazards associated with the finished product. Also, there may be hazards associated with processing a new propellant composition that have never been previously encountered. Therefore, essential information for insurance of safety must be obtained by working on a small scale and by exhaustive tests of the product before undertaking larger scale work. Whether a new propellant formulation is detonable or not should be established early in its development. The protection required in working with detonable propellants is substantially greater than in working with those which are not detonable.

Exhaustive product testing, while undoubtedly highly desirable, will reach a point of no return and, perhaps, before that point is reached, interpose an intolerable delay to larger scale production of more energetic propellants. Furthermore, the demands for more and more energetic propulsion require use of the most energetic ingredients compounded to take full advantage of their available energy. Under these circumstances it seems certain that explosions during processing cannot be immediately eliminated. Because such incidents must be accepted as part of first production, plants must be designed so that property damage will be tolerable and injuries to employees and loss of life will be prevented.

PURPOSE AND SCOPE

Safety requirements are prescribed that are intended to reduce the probability of property damage and bodily injury incidents during the manufacture and loading into rocket motors of castable composite propellants.

Those who are responsible for the design of propellant manufacturing facilities and for their operation should observe all the applicable admonitions presented in other sections of this publication. For the purpose of this publication, composite propellants are those which consist of mixtures of fuels, binders, and oxidizers with or without other ingredients. It is not applicable to operations involving only colloid propellants; however, it is applicable to colloid propellants (e.g., cast double-base) that are used as ingredients in composite propellant compositions.

Building Construction

- a. Maximum use shall be made of fire-retardant materials.
- b. Construction and materials should be such that the missile hazard will be minimized. At least one wall of each building, bay, or room in which fuel compositions and oxidizers are mixed and subsequent hazardous operations in the manufacturing process are performed shall be of blowout-type, offering a minimum of resistance to an internal explosion. Roofs also shall be of the venting type.
- c. Where multibay or multicubicle construction is used, means should be provided for limiting the spread of fire from bay to bay or cubicle to cubicle. In future construction, substantial dividing walls shall extend through the roof and roofs shall be independently supported over individual bays. In addition, void space between ceilings and roofs shall be kept to a minimum.
- d. Exposed interior surfaces of propellant operating buildings should be smooth, fire retardant, and free from cracks and crevices. Joints should be taped or sealed. When walls and ceilings are painted, hard gloss paint shall be used to facilitate cleaning and minimize impregnation of finished wall and ceiling materials. As a further aid to cleaning and to eliminate areas where explosive materials and other dangerous materials may accumulate, a curved surface should be provided where flooring and walls meet, and flush-type construction should be used for wall openings such as doors and windows.
- e. Drains and sumps - All drain lines handling propellant or explosive wastes shall be provided with sumps or basins of adequate design and capacity for the removal of propellants by settling. The drains shall be free of pockets and

have sufficient slope (at least one-quarter inch per foot) to prevent settling of propellants in the drain line before they reach the sump or settling basin where the propellants are to be collected. Sumps must be designed so that suspended solid propellant material cannot be carried beyond the sumps by the wash waters. The design shall allow sufficient settling time based upon the settling rate of the material and the usual rate of flow. The sump shall be constructed so that the overflow will not disturb any floating solids. The design must also permit easy removal of collected propellants, and for retention of those propellants which float on water until they can be skimmed off. Bolted sump tanks or other types of construction that permit the propellants to settle in obscure or hidden spaces are prohibited.

Care must be taken to avoid the possibility of deposition of propellants from sump effluent due to drying, temperature changes, or interaction with other industrial contaminations. When propellants which are appreciably soluble in water are handled, sweeping and other dry collecting measures shall be used to keep them out of the drainage system.

In all new construction subsequent to the date of this manual, drains between the source of propellant and the sump shall be troughs with rounded bottoms and with removable ventilated covers to facilitate inspection for accumulation of propellants. Waste liquids shall not be run into closed drains and sewers. Inspections shall be made periodically and the results kept on record. Drains and sewers containing propellant waste materials must not be connected in a manner to empty such wastes into the normal sewage systems.

f. Flooring shall be of non-sparking materials and conductive when required by paragraph 4207 of reference (21).

g. Control buildings must be designed and located to protect operators that will occupy them. Protection provided, wall between operator and operation (operational shield), shall be reinforced concrete not less than 12 inches thick. Concrete and reinforcing steel shall be as shown on drawings approved by the Bureau of Naval Weapons. Both faces shall be reinforced with rods at least one-half inch in diameter, spaced not more than 12 inches on centers horizontally and vertically, interlocked with the footing rods, and secured to prevent overturning. Rods on one face shall be staggered with respect to rods on the opposite face, and should be approximately 2 inches from each face. Concrete should have a designed compressive strength of 2,500 psi and should meet Corps of Engineers' specifications. Such an operational shield constitutes adequate protection for operations involving less than 15 pounds of detonable material,

when the nearest part of the explosive is at least 3 feet from the wall and 2 feet from the floor. A reinforced concrete wall 30 inches thick is satisfactory for protection against the effects of up to 50 pounds of a massed quantity of explosive or detonable propellant. When protection is required against up to 70 pounds of massed explosive or propellant, 36 inches of reinforced concrete is required. The adequacy of these operational shields, including thickness, size, fastening, and location should be proved by actual test with a minimum safety factor of 25 percent above the maximum charge before its use is permitted in regular operations. Subterranean control shelters should be used for protection of operators concerned with over 70 pounds of explosive or detonable propellant. A concrete top with interlocking reinforcing rods or other suitable protection cover installed over the heads of operators for protection from missiles is recommended. The mass of explosive or detonable propellant must be placed so that its long dimension is perpendicular to the shielding wall, at least 3 feet from the wall, and 2 feet from the floor. Operations and control shelter must be separated as required by intraline table of distances, Table 7.11, ref. 21. If view of remotely controlled operation is required, indirect means such as television should be used.

Electrical Equipment

(a) The type and installation of electrical equipment and wiring shall comply with the provisions of the National Electrical Code as modified herein.

(b) Electric motors, wiring, lighting fixtures, and other electrical devices should not be located in rooms or buildings containing dust from propellant, flammable vapors, or combustible dusts which may form explosive or flammable mixtures with air. When, for practical reasons, such installations are necessary, the equipment or device must be approved for use in Classes I or II hazardous locations and shall be dual rated if both hazards exist. If dual rated equipment is not obtainable and the hazard of one type of air contaminant is greater than the other, equipment approved for the more hazardous conditions should be used.

(c) When it is necessary to install lighting fixtures that are approved for use in Classes I and/or II hazardous locations, lamps which raise the temperatures of exposed surfaces above 228° F shall not be used.

(d) These provisions shall not preclude the installation and use of electrical grounding circuits and static grounds in propellants operating buildings.

Ventilation

(a) Adequate ventilation shall be provided for operations involving vapors or dusts which are either toxic or explosive in nature. Wherever practicable, use should be made of systems with intakes near the source of vapors or dusts. When ceiling exhaust is used, high ceilings will aid in keeping the concentrations of air contaminants low at normal working level.

(b) Air-conditioning and circulating equipment shall be designed to prevent air containing combustible dusts from being recirculated through the conditioning unit.

(c) Effective means should be provided at all duct openings at hazardous locations to prevent contamination of the duct during periods when the fan or blower is not operating.

Automatic Deluge and Sprinkler Systems

Automatic deluge and sprinkler systems shall be provided in accordance with the principles of design adapted to operational demands.

Confort-Type Heating Units

(a) Radiation is the most commonly used and preferred means for heating explosives buildings. The most suitable types of radiators are those with exposed radiating surfaces in the form of S-shaped smooth pipe or fin-type radiators so placed that they can be easily cleaned. Other type of radiators are acceptable, but are less desirable because of cleaning difficulties. Shielding or guarding should be used where radiating surfaces are so located and sufficiently hot to cause personnel injuries as a result of contact. If necessary for cleaning, shields or guards should be easily removable.

(b) Heating pipes may be embedded in walls (except substantial dividing walls) and floors. In the case of the floor installation, however, special care must be taken to assure that the floor is free from cracks, crevices, and other imperfections which will allow propellants to collect around the subsurface piping. In addition, consideration must be given to the design and operation of the system to assure that cracks, crevices, and other imperfections will not develop during operation as a result of expansion and contraction.

(c) Convection heating may be used, provided motors are approved for use in both Class I and Class II hazardous locations and fans are constructed of nonsparking material.

Grounding

Manufacturing equipment and conductive flooring shall be grounded in compliance with Chapter 42 of reference (21).

Lightning Protection

Lightning protection shall be provided in accordance with Chapter 41 of reference (21).

Operational Shields

(a) Operational shields, constructed as specified above, shall be utilized for the protection of employees, material, and equipment. Design of these shields shall be based on potential hazards involved. The shields as specified are mandatory if detonable propellants are involved. The specifications should serve as guides in the design of operational shields that are to provide protection from other types of hazards (e.g., fire, rupture of pressure vessels, and high-velocity high-temperature gas streams).

(b) The design of operational shields shall take into account the quantity of propellant involved, confinement that may be present, and the potential initiation hazard involved. Hazards that may be encountered in the processing of propellants include:

(1) Detonation of propellant.

(2) Fires involving unconfined propellant.

(3) Pressure failure of a vessel or case resulting in fragmentation (heavy wall cases, especially those of mild steel construction and operated at high pressure, can produce fragments of high energy that constitute a major hazard).

(4) Pressure failure of a vessel or case which results in no fragmentation (light wall motor cases constructed of aluminum or high-stressed steel are examples of vessels likely to produce this type of hazard).

(5) High velocity, high temperature gas streams (ignition of restrained composite propellant filled motors, with or without nozzles, and similar semi-confinement vessels are likely to produce this type of hazard).

(6) Motors, with or without nozzles, that are not adequately tied down may take flight upon ignition.

(c) In the absence of reliable data, the adequacy of an operational shield shall be proved by actual tests before its use is permitted. Results of such tests shall be made known to the Bureau of Naval Weapons.

(d) In designing operational shields, special attention shall be given to provision of means for adequate venting, based on the rate of hot-gas evolution in the event of an accidental ignition.

Establishment Layout

(a) Composite propellant manufacturing and motor loading operations shall be performed in a special area that is separated from all other areas and the boundary of the establishment by inhabited building distances, given in Tables 7.9 and 7.10, reference (21).

(b) Consistent with safety and efficiency, individual hazardous operations shall be separated from each other and from all operations which are not hazardous. Where operationally feasible, intraline distance separation, Table 7.11, reference (21), should be provided. When more than one hazardous operation is performed in a single building, maximum possible use should be made of substantial dividing walls and operational shields for separating the operations.

(c) Individual explosive buildings within a composite propellant operating line shall be separated from each other and from buildings not containing propellants (within the same operating line) by appropriate intraline distances. Except for service magazines and curing facilities, adjacent buildings housing explosives operations of different degrees of hazard must be separated by the distance required for protection against the most severe hazard. Service magazines and curing facilities must be separated from the individual operating buildings they serve by intraline distance, based on the quantity of explosives in the service magazines and curing facilities. Nonexplosives facilities (e.g., paint and solvent storage buildings) serving a single operating building may be located at less than intraline distance but not less than 100 feet from the operating building.

(d) Adjacent operating lines producing the same propellant must be separated by intraline distance specified in reference (21).

(e) Batch mixing operations must be performed in buildings used exclusively for that purpose. Small mixers may be located in buildings containing other operations, provided the mixer is in a separate bay with operational shields protecting all other operations from the mixing operation.

(f) In planning the location of new facilities that are intended for class 2B materials, due consideration should be given to the possibility that Class 9 explosives may be processed in future operations.

Explosives Hazard Classification

(a) Prior to use in propellant manufacturing processes, efforts must be made to determine the hazardous chemical and physical properties of individual raw materials and all compositions.

(b) The explosives hazard classifications assigned by this paragraph are applicable to operations involving fuels from which explosives are excluded, and oxidizers which produce propellant compositions that are not detonated in the following tests. Both cured and uncured propellant must be used in tests to determine their detonability. Confinement must be provided by placing the propellant in 8-inch schedule 40 pipe or a container of equal or greater diameter and comparable strength. The pipe or other container must be at least four diameters long (i.e., at least 32 inches long) and must have one end capped or welded to a metal base. The following initiators must be used for the tests:

Uncured Propellant

(a) Engineers' Special Blasting Cap with 30 grams of tetryl

(b) Squib and 2 ounces of black powder

Cured Propellant

(a) Engineers' Special Blasting Cap with 30 grams of tetryl only. The initiator must be placed one diameter above the base of the container, equidistant from the sides of the container. Suitable means must be provided for determination of reaction of the propellant to the initiators. Each type of test must be performed at least five times.

(c) If detonation or deflagration-to-detonation tests (b) above, reveal that the uncured propellant is detonable, casting and curing operations involving the propellant must be considered Class 9 explosives hazards. If detonation tests reveal that cured propellant is detonable, casting, curing, and all subsequent operations must be considered Class 9 explosives hazards.

(d) When warheads containing high explosives are assembled to rockets or missiles with motors containing propellant, tests must be conducted to determine the possible contribution of the propellant (expressed in terms of quantity of explosive required to produce same effects) to an explosion involving the warheads. Quantity-distances are based on the quantity of explosive in the warhead plus the explosive equivalent of the motor. Full scale tests are required.

(e) When warheads containing high explosives are assembled to rockets or missiles with motors containing Class 9 propellant, quantity-distances are based on the combined weight of explosives in the warheads and the motors.

Oxidizer Processing*

(a) General

(1) Safety regulations for the safe handling of oxidizing materials as given in Chapter 33, reference (21), must apply.

(2) Contamination should be avoided. Time of exposure, temperature, and moisture are factors that determine the permissible location or degree of use of metals and chemicals that can sensitize the oxidizer.

(3) Because of the danger of contamination of oxidizers all operators must be shielded from screening, blending, grinding, and mechanized drying operations by a 12-inch reinforced concrete wall or equivalent.

(4) Closed systems should be used where possible to eliminate dust and contamination from outside sources.

(5) Flexible connections (socks) in pipes or duct systems through which oxidizer materials are conveyed, should be fabricated of fire-retardant materials that are chemically

* Cf. prior discussion of oxidizing materials on page 36

compatible with the oxidizers to which they will be exposed. The pipes or duct systems shall be made electrically continuous. Flanged pipe connections shall be used in lieu of threaded joints wherever practicable.

(b) Drying of oxidizing agents

(1) The maximum safe temperature for drying each material shall be established and shall not be exceeded at any point in the drying apparatus or drying room.

(2) If the dryer is capable of attaining temperatures that exceed the maximum safe temperature for the material being dried, dual thermostatic controls must be used to prevent the established maximum temperature from being exceeded. Temperatures must be recorded. If non-recording-type thermometers are used, readings should be taken at regular intervals and a record of such readings should be made. Thermometers should be so placed that the maximum temperature in the drying room or drying apparatus will be indicated.

(3) Dust formation or accumulation must be eliminated.

(c) Screening

When screening is performed for process purposes, screening equipment shall be constructed to prevent the oxidizer material from being subjected to pinching, friction, or impact as a result of metal-to-metal contact. Rooms in which screening units are operated shall be thoroughly cleaned daily, or more often as necessary, to eliminate hazardous accumulations of dust.

(d) Blending of Oxidizers

If analyses indicate that gases are released during blending of oxidizer batches, a suitable means of relieving pressure shall be designed into the blender to prevent rupture.

(e) Grinding of Oxidizers

(1) When impact-type mills are used, sufficient clearance shall be maintained between stationary and moving parts to prevent metal-to-metal contact. Clearances shall be checked as frequently as necessary to assure continuing adequacy, but not less than once daily.

(2) Oxidizer material shall be passed through a screen and magnetic separator for removal of extraneous materials. The screen and separator should be located in the

intake of the grinder or pulverizer. Screen openings should be the smallest that permit free flow of the oxidizer.

Preparation of Fuel Compositions

(a) The design of equipment and methods of handling shall minimize the formation and accumulation of dust. If the material being processed is toxic or flammable, adequate exhaust ventilation and personal protective equipment shall be utilized.

(b) Compatibility of materials shall be established and controls shall be incorporated to preclude the mixing of materials at a time or in a manner that would result in sensitive compositions or hazardous conditions prior to process requirements.

Mixing of Fuel Compositions and Oxidizers (Batch Method)

(a) Mixing operations shall be remotely controlled. Operators shall be provided adequate protection against a potential explosion of the total quantity of materials being mixed. Not more than one production size mixer shall be located in a single building unless protective construction will assure that an explosion in one mixer will not damage other mixers.

(b) Oxidizer material must be introduced into the mixer in a manner that will minimize the formation of dust and static electricity.

(c) Effective means must be provided for preventing extraneous materials from entering mixers. When by reason of size, shape, process requirements, and the like, it is not possible to screen dry solids before they are charged into the mixer, and introduction in a slurry form is impossible, an inspection technique must be developed to prevent extraneous materials from entering the mixer. Consideration must be given to such devices as magnetic separators, fluoroscopes, and X-ray.

(d) Blades and other moving parts of new mixers must be carefully inspected ("Magnaflux", X-ray, etc.) for cracks, crevices, and other imperfections before being put into operation and periodically thereafter. Below clearances between agitator blades and mixer bowls must be determined frequently enough to assure continuing adequacy, but not less than once daily. A record must be maintained of mixer blade adjustments and evidences of damage to mixer blades and bowls.

(e) When consistent with process requirements, a non-combustible cover must be placed over the mixer bowl after charging operations are completed, to prevent the accidental introduction of foreign object into the mixer. This cover may be lightweight metal or screen with mesh no greater than the minimum clearances of the mixer blades. The cover must be so secured to the mixer housing that gases or vapors evolved during the mixing operation will not be confined and that exhaust will be afforded in the event of fire in the mixer. Hoppers and other means for charging mixers must not add to the confinement that is inherent in the design of the mixers.

(f) Spilling or splashing of propellant during discharge of mixers must be avoided.

(g) Only non-sparking devices may be used to scrape down the sides and blades of mixers. Positive controls must be established to prevent these and other devices from being accidentally introduced into the mixer.

(h) Means shall be provided for effective removal of toxic and flammable vapors, gases, fumes, and dusts from the mixing room.

Inspection must follow immediately after occurrence of any event which could cause cracks, a written record of inspection must be made and preserved.

(i) Operators shall be so stationed during discharge operations that direct, unblocked routes of rapid exit will exist for emergency use.

(j) Electric service to propellant mixers must be interlocked with fire protection system controls (i.e., heat actuated devices or electronic controls) to prevent operation of the mixer when the fire protection system is inoperative.

(k) Nuts and bolts on mixers, monorail systems, or in other locations that may loosen and fall into a mixer must be drilled and thonged or otherwise effectively secured to prevent such an occurrence.

(l) Uniforms of operators must comply with the requirement of Chapter 43 of reference (21). Objects such as jewelry, pens, pencils, coins, and rings that may accidentally be introduced into mixers must not be permitted in the building.

Casting Composite Propellant

(a) Casting vessels under pressure will be capable of withstanding at least twice the maximum allowable working pressure to which they are subjected. Periodic hydrostatic tests of such casting vessels must be performed at maximum intervals of 3 months. Hydrostatic tests must be made also after any alteration to the casting vessels. A log of tests performed must be maintained for each vessel. Similar tests must be made of vessels which are evacuated in use.

(b) Casting vessel assemblies must be designed without internal cracks, crevices, corners, and pockets and any internal mating configurations which could cause propellant in a thin film to be pinched or rubbed.

(c) Lids must be secured to pressurized casting vessels in such a manner that they will withstand the rated pressures of the vessels. Frequent tests must be made to assure that the locking device is functioning properly.

(d) Line pressure for pressurizing the casting vessel must not exceed the working pressure of the vessel. Filters must be installed in gas lines to remove water and oil.

(e) A blowout disk (designed to blowout at 120 percent of the vessel's maximum allowable working pressure but not more than 150 psig) must be provided. The design must take into account the potential rapid rise of pressure within the vessel due to ignition of the propellant.

(f) Means must be provided for preventing movement of the casting vessel when rupture of the blowout disk occurs.

(g) Valves through which uncured propellant flows must be designed to prevent propellant from being compressed between two metal surfaces (e.g., rubber diaphragm-type valves). These valves shall be cleaned and inspected at regular intervals suitable to the process and a log of these inspections must be maintained.

(h) When casting is performed by pump, rupture sections must be installed both at the inlet and discharge sides of the pump. These rupture sections must be designed to relieve pressures in case of fire in the pump.

(i) When mandrels are inserted mechanically, the equipment must be designed to prevent metal-to-metal contact between the mandrel and the motor case below the propellant surface.

(j) When pumps are used, adequate protection must be provided for the workers engaged in operations at the propellant casting station. If the transfer vessel and pump are at the propellant casting station, casting must be performed remotely with operators suitably protected from the exposure.

Propellant Curing

(a) The safe temperature for curing the propellant must be established, and dual heat controls must be installed to prevent that temperature from being exceeded.

(b) Heating units or elements must be designed to eliminate any direct contact between the heating unit or element and the propellant.

(c) Loaded motor cases or casting molds must be handled or secured so that overturning will be prevented.

(d) Means of pressure relief must be provided on closed pressurized vessels into which motors are placed for curing.

(e) Mold supports and other casting and curing fixtures should be designed to avoid rubbing or pinching of thin layers of propellant between metal surfaces.

(f) Loaded or partially loaded rocket motors must be raised or suspended at minimum distances above floor level. If tests or experience indicate that rocket motors may ignite upon dropping, protective measures must be employed to prevent ignition.

Motor Finishing and Assembly

Detonable propellants and motors containing detonable propellants may only be machined by remote control.

(a) Securing Motors

When operations are performed on cured propellant contained in pressure vessels or rocket motor cases and there is a possibility of ignition, the vessel should be secured in fixtures capable of withstanding the rated thrust of the assembly (based on its performance as a rocket motor) with a safety factor of 2.5 to offset shock loads.

(b) Threads

(1) Where the design of a motor case incorporates internal threads, means must be provided for preventing contamination of the threads with propellant.

(2) Whenever possible, the design of casting and curing assemblies and fixtures must exclude internal threads, cracks, and crevices where propellant may be deposited.

(3) All threads must be cleaned and inspected prior to assembly of component parts.

(4) Assembly of threaded components should be accomplished by remote control with operators protected by adequate shielding if a possibility of propellant contamination exists.

(c) Mandrel Removal

As a minimum, freeing of the mandrel must be a remote control operation with operators provided protection from a potential incident involving the motor.

(d) Machining of Case-Bonded Propellant

(1) Case-bonded composite propellant may be cut, drilled, or otherwise machined in a vertical or horizontal position. The most desirable position from both the operational and safety viewpoint must be determined locally.

(2) Design of the machining area and equipment must take into account the severe hazards of finely divided propellant, must provide adequate protection for operators, and be capable of minimizing damage in event of an incident. Finely divided propellant and propellant dust should be removed by means of a vacuum collection system, preferably of the wet type, with the intake point as close as possible to the cutter blade.

(3) Machining equipment must be designed to prevent contact of cutting tools or blades with motor cases and other metal objects, to eliminate the generation of excessive heat, to facilitate removal of dust and chips, and to afford personnel protection. Design points to be considered in attaining these criteria include: configuration of tool, lineal and rotational speed of tool, tool metal, rate of tool feed, alignment of tool, control devices, power

source, maintenance or replacement of tools, safe and effective coolants, and dust and chip removal. The characteristics of individual propellants to be machined must be considered in machine design because of differences in their physical properties and initiating characteristics (e.g., propellant exhibiting elastic properties may require greater rotational speeds and rates of feed than brittle material).

(4) When exhaust systems are used for removal of dust and chips, they must comply with requirements of volume 2 of reference (21). Waste products may be removed by immersion in a stream of water flowing away from the operation and collected at a point outside the operating room or cubicle. If the design of the motor or grain or the need to reclaim the propellant waste preclude the use of either of these methods, waste products may be collected in a dry state at the operation. The quantity of waste collected at the operation (when added to that quantity in processed and unprocessed motors in the machining room or cubicle) must not exceed the total weight of propellant in the maximum number of unprocessed motors permitted in the room or cubicle.

(5) Operator and material limits for machining rooms and cubicles must be determined in accordance with the principles outlined as follows:

The cardinal principle to be observed in any location or operation involving explosives, ammunition, severe fire hazards, or toxic materials is to limit the exposure of a minimum number of persons for a minimum time, to a minimum amount of the hazardous material consistent with safe and efficient operations. All operations must be scrutinized to devise methods for reducing the number of people exposed, the time of exposure, or the quantity of material subject to a single incident. Determination of operator limits requires that, first, jobs not necessary to a particular hazardous operation not be accomplished there; second, unnecessary workers not be permitted to visit the location; and third, too many consecutive operations not be permitted in the same room or building without adequate dividing walls, fire walls, or operational shields, depending upon the nature of the hazard. Personal limits must allow for necessary supervision and transients. Key employees should be appointed as monitors to assist in enforcing the established limits.

Determination of limits for hazardous materials requires a careful analysis of all facts including operation timing, transportation methods, size of the items, and the chemical and physical characteristics of the material. More strict limits are required for the more sensitive or more hazardous

materials. Limits must be established for each operation rather than on an overall basis so that each worker may be charged with the responsibility of not exceeding the established limit. Limits need not be expressed in units of weight or in the number of items as such. They may be given in terms of trays, boxes, racks, or any other unit which may be more easily observed and controlled. Explosive limits should not be established on the basis of the maximum quantity of explosives allowable, as defined by the existing quantity-distance separation to nearby exposures, when lesser quantities of explosives will suffice for the operations.

All rooms, cubicles, and buildings containing hazardous materials must have posted in a conspicuous place a placard stating the maximum amount of the material and the maximum number of workers and transients permitted in the room at any one time. In addition, other placards must be posted to set forth important local regulations as needed. Workers and materials limits and the placards must be kept current. The supervisor, foreman or worker-in-charge must prevent accumulations of excess materials, and when found, any excess should be removed immediately. Likewise, proper steps should be taken to have excess people, when found, leave the premises. The people and quantity limits for buildings or process divisions must be recorded on a plant layout and maintained on file.

(6) Drilling of rejected motors for the purpose of reclaiming the propellant or motor case must be performed in an isolated location. Operators must be protected by operational shields and/or distance.

(e) Machining Non-Case-Bonded Propellant Grains

(1) Propellant grains that are not case-bonded should be machined to the extent necessary before they are loaded into motors.

(2) Insofar as they are applicable, the requirements in (d) above for machining case-bonded propellant also must be met when machining composite propellant grains that are not case-bonded.

(f) Igniter Insertion

(1) The following requirements apply where the design of a motor makes it necessary to insert the igniter within the manufacturing line:

(a) The supply of igniters at the insertion station must be the minimum consistent with safe and efficient operation.

(b) If removal of the shorting clip is required by the process, the igniter must remain shorted until immediately prior to insertion.

(c) Process storage facilities that are vented to the atmosphere and designed to withstand the effects of an incident involving all igniters therein should be provided.

(d) Means must be provided for grounding operators for dissipation of static electric charges during igniter insertion.

(2) Electrical continuity tests for igniters that are in motors must not be performed in the propellant manufacturing and motor loading line. Such tests must be performed in a separate facility, by remote control, with the operator provided protection from a potential incident involving the motor.

(g) Materials Handling

(1) If loaded motors containing cores must be moved, the core and motor case must be supported by or suspended from a common source or in some manner locked or tied together to prevent independent movement of either.

(2) A comprehensive preventive-maintenance program must be instituted for equipment used to move motors loaded with composite propellants.

(h) Disassembly

Disassembly operations involving assemblies and fixtures that have internal threads, cracks, and crevices where propellant may be deposited must be performed by remote control, with operators protected by adequate shielding

(i) Painting and Marking

Spray painting operations must comply with the requirements of volume 2 of reference (21).

(j) Reworking

(a) Loaded components disassembly operations must be separated from other operations. Common facilities may be used for assembly and disassembly operations, provided the operations are not performed at the same time.

(b) Reworking of defective loaded components must be accomplished only by properly trained operators under the

direction of supervisors who are fully aware of the hazards involved in both assembly and disassembly operations.

(c) Operators must be suitably protected during disassembly operations involving the removal of pyrotechnic-type igniters.

(k) Collection and Disposal of Hazardous Waste Materials

(a) Waste collection and disposal activities must be closely supervised and prescribed by standard operating procedures.

(b) Waste materials must be removed at regular and frequent intervals from all operating areas. Cured propellant scrap should be kept under water and should not be allowed to accumulate in quantity at operations.

(c) Separate, properly labeled containers should be used for the different types of waste encountered (e.g., combustible waste, waste propellant, waste oxidizer, and oily rags).

(d) Waste material disposal must be in accordance with requirements of Part IV of reference (21).

(l) Protective Clothing and Equipment

(a) Employees whose clothing may become contaminated with oxidizer or propellant must wear clean garments. Clothing must be changed as often as is necessary for safety. Garments must be made of tightly woven smooth fabrics treated with fire-resistive chemicals, must be equipped with non-metallic fasteners, and must be easily removable. Pockets, if any, must be of skeleton-type and trousers must be without cuffs. Silk, wool, rayon, or other materials known to produce static electric charges should not be worn. Personal hygiene should be encouraged. Persons exposed to flammable or toxic materials should be required to take a shower at the end of each shift.

(b) Employees should be inspected when leaving the change house or prior to entering the work areas in order to be certain that each person who enters a hazardous area is properly clothed and wearing suitable footwear.

(c) Persons regularly employed in propellant operating buildings must wear non-sparking footwear. All persons entering areas in which conductive flooring is installed should be equipped with conductive safety shoes meeting the requirements of Chapter 43 of reference (21).

(d) Persons employed in dusty atmospheres must be provided with and required to wear respirators of a type approved by the U. S. Bureau of Mines for use under specific existing conditions. The dust concentration, expressed in milligrams per cubic meter of air, must determine the necessity for such equipment.

(e) Flame-proof head coverings should be worn where there is a concentration of oxidizer dust.

(m) Maintenance

Proper maintenance on a regularly scheduled basis is essential to safe operations. Regular schedules for checking, adjusting, and repairing operating equipment must be established. Only trained and competent operators shall adjust, clean, and repair propellant operating equipment.

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U. S. NAVAL ORDNANCE LABORATORY

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ation is changed as follows:

Page 5, line 1, evolution instead of evaluation

Page 5, line 23, " " " "

Page 6, line 27, should read (1905-1944)

Page 6, line 28, should read (1952-)

Page 7, line 29, insert not after can

Page 7, line 29, delete word all

Page 10, Title - correct spelling of Important

Page 46, Item 68, should read Sodium Nitrite

Page 64, line 12, insert of instead of or

Page 73, line 6, correct spelling of critically

Insert this change sheet between the cover and the title page

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EXPLOSIVES, PROPELLANTS AND
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LABORATORY, PILOT PLANT, AND
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EXPLOSIVES, PROPELLANTIC AND PYROTECHNIC SAFETY COVERING
LABORATORY, PLANT PLANT, AND PRODUCTION OPERATIONS

By:

Russell McGill

Approved by:

D. C. Hornig
D. C. Hornig, Chief
Chemical Engineering Division

ABSTRACT: Precautions, admonitions, warnings, and instructions for the safe performance of laboratory experiments, operation of semi-works, and first stage production in plants are given in this report. It may be used as a safety manual in connection with any or all of the actions mentioned. Alternatively, it may be used as the basic text for use in writing a safety manual for a specific establishment where in high energy chemicals and compositions are manipulated.

PUBLISHED FEBRUARY 1962

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

27 October 1961

This report was written in compliance with a request from the Bureau of Naval Weapons for textual material for a manual to be used in connection with all kinds of work with high energy materials; explosives, pyrotechnics, propellants and related materials from the first small scale laboratory experiments through the first stages of production. Alternately, the report, itself, may be used as a manual.

The work was done under the Bureau of Naval Weapons task number NUME-3E-000/212-1/F008-10-004, problem assignment number 012, Study of Explosives Properties.

In addition to the Naval Ordnance Laboratory, four other Naval activities made contributions on assigned topics: the Naval Ammunition Depot, Crane, Ind.; the Naval Ordnance Test Station, China Lake, Cal.; the Naval Propellant Plant, Indian Head, Md.; and the Naval Weapons Station, Yorktown, Va. Part of the texts of these contributions have been incorporated. Nearly all the contributed material which was not so used was integrated throughout the report. In the latter cases it is impractical to identify and to indicate each specific credit. These contributions were definitely helpful whether used intact or throughout the text. All contributions were gratefully received.

The assistance of private industrial establishments was solicited. These organizations, mostly Department of Defense contractors, were asked to furnish their safety manual or safety instructions issued in other forms such as letters, memoranda, or operating procedures. The following made contributions in response to the requests.

Aerojet-General Corporation
Amcel Propulsion, Incorporated
Caliery Chemical Company
E.I. du Pont de Nemours & Company
Hercules Powder Company
Holston Defense Corporation
Midwest Research Institute
Olin Mathieson Chemical Corporation
Phillips Petroleum Company
Rocketdyne, Incorporated
Thiokol Chemical Corporation
Wyandotte Chemical Corporation

W. D. COLEMAN
Captain, U.S.
Commander

ALBERT LIGHTBODY
By direction

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EXPLOSIVES, PROPELLANTS AND PYROTECHNIC SAFETY COVERING
LABORATORY, PILOT PLANT, AND PRODUCTION OPERATIONS

INTRODUCTION

This report is being written to supply complete general instructions for safe operations with high energy compounds, explosive or propellant, from very small laboratory preparation through full scale production for use. While both industry and the U.S. government have been the source of many publications on explosives safety, none of these have been uniquely devoted to the sequence of operations required to develop new compounds and new compositions through manufacture for production.

The conclusion that there is a need for such a treatise on safety in the later stages of development of high energy compounds and compositions, may be developed by another reasoning process. The research worker who accomplishes the initial synthesis of a high energy compound or initial high energy compositions will achieve safety by operations with very small quantities. This small scale operation will be repeated. Since the operation is with small quantities, perfect protection by remote control or shielding can be established. There is no specific experience to guide the experimenter to assurance of safety in these initial experiments.

The initial small scale experiments will be repeated until a sufficient amount of material has been obtained and used for preliminary testing and evaluation. The information gained by these experiments may justify recommendation of a larger scale evaluation. The experience gained in these initial experiments must be used to insure the safety of those undertaking more advanced work. In case the work with larger quantities of the experimental high energy substances is undertaken by persons who have not done the initial small scale experimental work, complete knowledge of the first experience must be acquired. In other words those who undertake large scale work must be advised and required to learn All the experience obtained in All earlier work. There is no doubt that a considerable reduction of accidents and incidents would result if all workers with explosives and propellants were to follow absolutely the admonition of the previous sentence. Reference (1) seems to support this conclusion by the statement therein that the major causes of explosive accidents in research, development, test, and evaluation work are: improper or inadequate operating procedures or processes; failure to observe regulations; or failure to understand hazards.

The FIRST ACT of those who increase the scale of any of the following operations beyond small scale laboratory experiments,

MUST BE TO LEARN EVERYTHING KNOWN ABOUT THE EQUIPMENT USED, THE CHEMICALS, THEIR INTERACTIONS, AND ALL EXPERIENCE OF PRIOR WORKERS.

1. Laboratory preparation of high energy compounds and compositions.
2. Laboratory preparation of pyrotechnics and incendiaries.
3. Pilot (semi-works) manufacture.
4. Pilot (semi-works) loading.
5. Production manufacture.

The increase in scale may be made by the identical workers who did the first small scale work. The scale may be increased by others at the same establishment. In this case those who undertake any of the operations enumerated above can very conveniently consult those who have the pertinent experience. They can be consulted as often as may be necessary.

The procedures prescribed herein are to be followed when any of the above operations are concerned with any of the following:

1. Initiators or primary explosives.
2. Boosters.
3. High (secondary) explosives.
4. Propellants.
5. Pyrotechnics and incendiaries.
6. High energy intermediates.

The word explosives, the expression high energy materials, or obvious equivalents thereof used herein, will be understood to include all or any of the list immediately preceding.

While the admonition to obtain all pertinent prior experience before undertaking similar operations will usually be in contemplation of larger scale operations, this is not always true. New operations with compounds or compositions which are not new may be concerned with equal or smaller quantities than those of prior operations. Even though the scale of operation is not increased or is decreased those who have not previously worked with the compound or composition must learn about all the public published information, classified information, and unreported or privately record experimental experience.

The previously obtained experience and knowledge may not be available at the installation where additional work is to be done. If the work was done at another Naval or Department of Defense installation, it will be necessary to obtain all the experience and reports from the other installations. This should be done by study of reports first and then almost always it will be necessary to confer at least once with the previous workers. Such conferences among other details, may elicit news about incidents that were harmless but which under other circumstances, may not be harmless and may cause personal or property damage. Such incidents should be thoroughly investigated and all details reported fully.

Knowledge of British or Canadian experience can be obtained from their reports or through their service missions in Washington, D.C.

If prior work was done in a U.S. Government installation but the experimenters have left Civil Service they may be employed on government sponsored research at a private establishment. In this case it should not be difficult to arrange conference time with the scientist or engineer whose experience is needed. Furthermore, private employers can usually be expected to cooperate fully in allowing their employees to give the government the benefit of their experience. This cooperation may be had without pay but arrangements can be made for government reimbursement, if required.

In summary, knowledge of previous experience with high energy compounds or systems can be obtained under any conceivable circumstances. In most cases such information is essential to safety of operations on a larger scale. Therefore, it is strongly recommended that pilot plant employees seek information and counsel from the laboratory or person, irrespective of employment or location, having knowledge of the manufacture of the high energy material in question.

It is also strongly recommended that the user seek information from the laboratory or person, irrespective of employment or location, having detailed knowledge of the properties of the high energy material in question.

The characteristics of intermediate compounds of any synthesis must be known and understood as intermediates may be more likely to be dangerous than the product. Furthermore, conditions during any synthesis are more favorable to violent reaction or even explosion than the conditions after the synthesized compound has been isolated as a pure explosive.

In summation, these advices require all workers with high energy compounds and compositions* to learn and understand the experience of all those who have any knowledge of the compound, composition, or process involved. Furthermore, if possible, a demonstration of synthesis or process by experienced person or persons should be arranged. Such demonstrations will complement the information from persons and reports. Following the demonstration by experienced persons a rehearsal with inert materials should be carried out by those who will increase the scale of operations and, if they are inexperienced with the specific compound or operation, even if the scale is not increased.

So far only very general admonitions have been given. The considerable amount of detailed information about laboratory, pilot plant, and plant hazards have not been mentioned. More detailed statements of safety principles, personal responsibility for safe operation, and explanation of origins of hazards are given in the following text. These nearly all involve chemicals or chemistry because the hazards of work with pyrotechnics, propellants, and explosives are caused by chemicals and their chemistry.

Section 10 of reference (2) is highly recommended as a comprehensive source of information about the hazards of 9000 chemicals or compositions. The bibliography of Section 10 is given herein as Supplement A for the convenience of the user of this publication. It should be noted that chemical manufacturers supply much information about their products.

Those who intend to undertake the production of an explosive or other high energy compound or composition are most emphatically urged to collect records of all the experience concerning the compounds or compositions to be produced. Now those who wish to insure that a group or sequence of acts are performed without omission make use of check lists. Therefore, in order to insure that all sources of information and experience about high energy compounds or compositions are consulted, a check list should be made. A specimen check list is included as Supplement B. However, each activity is advised to prepare their own list for their specific situation.

First items on the list should be the thermodynamic properties of the compound or composition to be produced. In fact, the thermodynamic properties will indicate whether or not the compound is a potential explosive. Any compound or composition which is capable of a spontaneous

*High energy compounds and compositions are to be understood, by readers of this report, to be compounds or compositions which will release more than about 800 calories per gram by burning or explosion.

change with the evaluation of a large amount of heat is potentially explosive and should be treated as an explosive. Heats of combustion, detonation and formation and free energy of formation are useful as standards for judging whether a compound or composition may explode. These data are available in references (3) through (8).

Heats of formation given in the literature are conventionally marked positive if heat is required to form them from the elements and negative if heat is lost to the surroundings during formation from their elements. For example, acetylene contains more energy than the carbon and hydrogen required to synthesize it. To synthesize 26 unit weights of acetylene requires 24 unit weights of carbon and 2 unit weights of hydrogen. The heat content of elements, carbon and hydrogen is conventionally zero. The heat content of 26 unit weights of acetylene is +54.19 kilocalories. Therefore, the heat of formation, designated H_f , is +54.19 kilocalories. This heat energy may be obtained by decomposition of acetylene and can be released explosively under favorable circumstances. Considerable additional energy can be obtained by oxidation of the carbon and hydrogen so released. The algebraic sum of the energies from the two sources is the heat of combustion. The heat of combustion of acetylene is 332 kilocalories per 26 grams. The reverse of the conventional use of signs, as stated in the first sentence of this paragraph, is sometimes followed. Therefore, the reader is advised to make sure which sign is used to designate absorption or evaluation of heat during formation of any compound from its elements.

If heats of combustion or formation are not available in the literature these may be calculated from bond energies. These calculations are not difficult. They are discussed and examples of calculations given in reference (7).

The collection of thermodynamic information will be a part of the comprehensive survey of literature information about the specific explosive compound or composition. Literature surveys must be comprehensive in both time and space. The sources of literature of various nations have been collected and described in reference (9) which is truly a guide to the literature. There are several classes of literature that must be searched if one is to be sure of finding all the public literature. Undoubtedly, the most comprehensive source is Chemical Abstract which was first published in 1907. Beginning with 1907, emphasis has been placed on complete inclusions of the world's chemical literature. Searching Chemical Abstracts can be done expeditiously because of the author and subject indices which have been published annually and decennially. British Chemical Abstracts, established in 1926, is another abstract journal in English. Chemisches Zentralblatt, established in 1830, is valuable because of its early appearance. Zentralblatt was spelled Centralblatt from 1856-1897. In 1919, the abstract section of Angewandte Chemie was merged with Chemische Zentralblatt. The reader

is urged to consult reference (9) for a more complete description of these abstract journals and their scope. Many other general chemical and specific abstract journals are listed and described in reference (9).

The abstract journals publish short summaries of other publications. While abstractors endeavor to include all information ... the abstracts they write, it is inevitable that condensation results in omission. Therefore, finding the abstract is a step in finding the original document which should be procured for study. Abstracts journals, such as Chemical Abstracts, endeavor to include all abstracts of chemical articles, books, and patents. The Chemical Abstracts Service publishes, quinquennially a list of all publications which have been or are being abstracted. The most recent list was issued in December 1956. Therefore, it is expected that a revised list will appear late in 1961.

It should not be assumed that failure to mention hazards connected with the synthesis or production of any compound or composition means that there are no hazards connected with the synthesis or production of any high energy compound or composition. Production on a small scale or in dilute solution may not have been dangerous. Also, workers may not have appreciated the dangers. For these reasons and others, warnings were omitted from the publication. Therefore, all workers with high energy compounds are emphatically warned against complaisance based on absence of warning in publications.

The older publications should not be neglected. Compounds or compositions may be thought to be new because no work with them has been done for many years. Memorial des Poudres, which was established 1882, is one of the few journals devoted to high energy material. Another is Zeitschrift fur das gesamte Schieß- und Sprengstoffwesen (1906-1904). This has been continued under another name, Sprengtechnik (1952). References (10) and (11) are texts on the earlier literature on explosives.

Those who propose to mix chemicals in order to obtain high energy compositions should learn about the chemical reactivity of each chemical. They should examine the literature to find reactions which may occur in the proposed composition or which may suggest similar reactions which may occur. The purpose of this literature search may be made clearer by an experience at the Explosive Research Laboratory of the NDRC Division 8 during WW II. The inclusion of lead peroxide in TNT charges for depth charges had been suggested in order to make the depth charges sink faster and to obtain other improvements. The stability of the compositions and compatibility of lead dioxide and TNT was investigated by heating one-half to 2.5 gram samples for 5 hours at 135°C. The results of these tests indicated compatibility and stability. Research work was continued, therefore, until arrangements were made to load a depth charge at the

Naval Mine Depot at Yorktown, Virginia. On the day before this cast loading, the investigator at the ERL decided to make another 100-200 gram batch of the composition. This one ignited while being melted on the steam bath. It was admitted, with considerable embarrassment, that lead dioxide is not suitable for admixture with TNT.

There are three lessons to be learned from this incident. First, that no stability test should be relied upon until the identity of the decomposition products has been established and that they can be detected by the stability test. Correlation with other tests such as explosion temperature and temperature of slower decomposition should be established. A test which would respond to gaseous acidic or reducing products was used to test the lead dioxide-TNT composition. Absence of these specific compounds as decomposition products did not prove stability as was assumed. Second, stability tests of a few grams of material cannot be applied reliably to quantities of over 100 grams. Third, had the person who suggested the inclusion of lead dioxide been thoroughly familiar with the chemistry of lead dioxide he would not have suggested using it with an organic explosive such as TNT. The reactions of lead dioxide as described in a treatise on inorganic chemistry such as either references (13) and (14), indicate clearly that lead dioxide is capable of igniting and oxidizing several classes of compounds at temperatures slightly above ambient. The conditions under which these reactions take place are sufficient reasons to expect the lead dioxide-TNT combination to have very poor stability. Reference to source books should be made before suggesting or accepting new compositions. Furthermore, even though one believes himself to be thoroughly familiar with the chemicals in question he should review their chemistry before undertaking work with them or compositions containing them.

The information sources mentioned above and others suggested in reference (9) can be expected to furnish all of the public information about high energy compounds or to indicate where such information may be found.

Much, and in some cases, all the information about high energy materials is classified, available only in Department of Defense Libraries and in possession of Department of Defense facilities. Probably the most extensive collections of classified information are at the Naval Ordnance Laboratory (NO), Picatinny Arsenal, the Bureau of Naval Weapons Library, the Armed Forces Technical Information Agency (ASTIA), and the Solid Propellant Information Agency (SPIA). Reference (12) contains information about the organic explosives reported before 1944. This compilation was recently declassified and is now freely available from the Library of Congress (photocopy or microfilm). A specimen check list for literature search is given as Supplement B.

Another form which may be used to establish that a proposed operation is either not hazardous or that adequate safeguards can be established is attached as Supplement C.

It is essential to safety to have all information about a given high energy material before undertaking production. It is also essential that the immediate supervisor of the operation be mentally capable of using the information. Therefore, work with high energy compounds or compositions must not be undertaken by anyone who is mentally fatigued. It is highly advisable that physical fatigue be considered as forbidding such work, also, as mental fatigue usually accompanies physical fatigue. Those who are mentally fatigued are less able to prevent occurrence of dangerous situations or to manage them safely if they do occur. It is well to arrange work with high energy materials so that it will be completed during the first six hours of the working day. The worker with high energy materials is strongly advised to disqualify himself during periods of mental or physical fatigue. This also applies to periods of mental stress or distraction.

RESPONSIBILITY OF SAFETY

Basic

The primary principle of safety is that all personal injuries are avoidable. This is meant literally and completely. It is perfectly practical for a good-size research laboratory to operate for fifty years without a single major injury. Several laboratories are already up to twenty-five years of this kind of success, and still going strong.

The Navy goes to great lengths in the way of safety devices, safe methods of construction, and general safety-mindedness on the part of management and line supervision. It is desired and expected that each research employee will also become fully convinced of safety thinking, as this is the only way in which injury-free performance can be realized. It is a complete impossibility to bring about a "fool-proof" physical environment and set of rules, a setting in which no injury can happen. Personal safety depends on sincere safety-mindedness and good judgment on the part of each individual, not at occasional intervals, but continuously as an integral part of daily activity. This is so in research even more than in any other type of work, since research by definition repeatedly involves things never done before.

It is our experience that the safety-consciousness of most new technical employees needs to be developed. It is commonplace to find many shades of fatalism, exemplified in such pat expressions as "accidents are bound to happen". All these are in our judgment simply rationalizations for indifference or bravado. Our conviction is that all injuries are caused, by specific carelessness or poor judgment on the part of someone.

This guide to safety in research and pilot-plant work is based on the premise that each individual worker must be the major factor in his own safety and that of his neighbors. The intrinsic hazards of research are manifold. In this guide we have compiled as general background the experience of thousands of man-years, particularly with reference to less obvious hazards. We expect every worker to be thoroughly familiar with this subject-matter, and to make daily use of it. It is also important to remember that even this vast amount of experience may still not include all situations. It is, and will continue to be, essentially evolutionary rather than having finality and absolute completeness.

Supervisory

Responsibility for safety follows the line organization. Each individual up to and including the highest ranking official is personally responsible for freedom from injuries to himself and all those who report to him. Safety responsibility cannot be delegated. This means that a superior is not exonerated from responsibility on the basis of poor judgment, carelessness, or disregard of instructions on the part of a subordinate. Each superior must feel that it is up to him to insure that his men are educated and supervised on safety. He must simultaneously promote safety by persuasion and by force of authority.

The function of safety committees is primarily suggestive, advisory and inspirational. All of the responsibility is directly in the line organization. No action or inaction on the part of any committee is to be construed as relieving any line worker from direct personal responsibility for safety.

MANDATORY SAFETY RULES

The following safety rules must be followed in all laboratory and semi-works areas.

1. Horseplay and practical jokes are strictly forbidden.
2. Approved safety spectacles are the minimum eye protection required in all laboratory and semi-works areas. Observe this rule yourself and insist that others in your area also observe it.

3. Do not eat, drink, or bring food into laboratory, semi-works or other areas where chemicals are handled or stored.
4. Observe rigorously the no-smoking rules of any area in which you may be.
5. Observe all warning signs in the area. In case of special hazards, be certain that adequate warning signs are in place.
6. Avoid unnecessarily distracting the attention of or startling any person engaged in laboratory work, especially hazardous laboratory work.
7. Laboratory work outside of regular working hours, without having a second person within hearing distance is prohibited.
8. Access to exits, safety showers, extinguishers, and controls must be kept clear at all times.

IMPORTANT GUIDING PRINCIPLES FOR SAFE WORK

The following general principles of safety are to be observed by all. In contrast with those of the foregoing section, which must be followed literally, most of these require exercise of good judgment in their interpretation and application. Any obvious neglect of or seeming indifference to these principles will be construed as a major performance deficiency of an employee.

1. Familiarize yourself with the contents of this safety manual. Be particularly certain that you have read and understood the section applying to any new work which you are undertaking.
2. Know the location and use of all emergency equipment in your area.
3. Familiarize yourself with the types of protective devices which are available for work under special hazards. Make use of the appropriate ones in each case.
4. Maintain your working area in a neat and orderly condition at all times. Point out and have corrected items of poor housekeeping outside of your own area.
5. Be alert to unsafe conditions and especially to unsafe actions. Call attention to these conditions and take action immediately and remedy at once, if possible.

6. Aim to avoid emergencies by careful thought and planning of your work. This planning should include foresight as to your own action in case an emergency does occur.

7. Anticipation of possible hazards depends to a large extent upon experience. In the planning of your work, seek the advice of men experienced in the field.

8. Remain out of the area of a fire or personal injury unless you can take an active part in meeting the emergency. Keep other curious bystanders out as well.

9. Think, act, and talk "Safety" until it becomes your best habit.

10. Familiarize yourself with, and abide by, all applicable safety rules of areas other than your own to which your work may take you. When entering a strange area, make yourself known to the individual in charge of that area.

11. Report all personal injuries and fires promptly.

COMMONPLACE HAZARDS

Although this manual is aimed primarily at safety in the laboratory, pilot plant and production areas, it is to be remembered that injuries can and do occur outside these areas. It is equally important to practice safety in offices, in halls, or stairways, and in other places where our daily activities may take us. Here safety is largely a matter of common sense, and requires little if any special knowledge. What it does require is a constant awareness of the common every day hazards to which we all may be exposed. The most common of these are the hazards of tripping, falling, bumping into protruding objects, or being struck by moving objects.

Fortunately, once we have truly acquired the habit of safety-mindedness, it will automatically govern our actions wherever we may be. Most of the safety practices that we follow routinely at work can be applied equally well off the plant. An off-plant injury can be painful, costly and inconvenient not only to the individual but also to his family. Our best protection is to be sincerely safety-minded at all times.

SAFETY EQUIPMENT

We list here for reference various types of safety equipment which may be procured and used by the individual workers. Many of these items are also mentioned in other sections of this manual, but for the sake of completeness we note in this section in a very brief way the primary purpose of each.

Eye and Face Protection

Protection of the eyes and face is necessary whenever there is a possibility of injury from liquid splashes or flying particles. Goggles must be carried in all Semi-Works operating areas. Safety spectacles must be worn in all research laboratory areas and Semi-Works operating areas.

Eye protection is of paramount importance in the safety program for two reasons: (1) the eye is irreplaceable, and (2) the eye, far more than any other body area, is susceptible to serious injury by relatively small amounts of chemicals, flying particles, heat or radiation.

Eye protection is required in all hazardous research and semi-works areas. This applies to all personnel, including supervision, clerical and stenographic help, janitors, craftsmen, and visitors. Eye protection is also required in certain hazardous plant areas.

Hazardous areas include any location where chemical, mechanical, or manual work is in progress or where chemicals are stored or handled. The principal hazardous areas are provided with "eye hazardous area" signs to serve as reminders, particularly to those not familiar with the area. Since eye hazards may also be present in unposted areas, constant vigilance is required. In case of doubt, eye protection should be worn until supervision can be consulted.

In many cases office desks are located in or near hazardous areas. Eye protection is required at such desks unless they are separated from the hazardous area by a partition at least 7 feet high. It is recognized that chances of eye injury are much less at a desk than at a laboratory bench. However, the risk that does exist, together with the likelihood that a person will neglect to put on spectacles when he leaves his desk, is the basis for requiring eye protection in unprotected desk areas.

Minimum allowable eye protection for employees is provided by safety spectacles, which have hardened lenses. This applies to all employees whether they normally work in a safety spectacle area or are just visiting such an area. Such spectacles, whether plain or prescription, are furnished and, if necessary, are fitted by an optician to insure maximum comfort.

The hardened glass lenses of safety spectacles are seriously weakened by scratching. Care should be used in handling spectacles in order to avoid scratching. They should be kept in cases when not in use. Safety spectacles with scratched lenses should not be worn; they should be replaced promptly.

Minimum allowable eye protection for visitors is provided by plastic spectacles of approved design. In areas where employees are required to carry or wear goggles, visitors are also required to do so.

Safety spectacles provide only the minimum eye protection; they are no time to be considered replacements for goggles, which are needed for protection against splashing liquids, fumes, dusts, flames, or particles approaching from the side. It is the responsibility of supervision to determine when goggles or other protective devices are required. Welding goggles, glass blower's spectacles, face shields, and other devices are available for specific jobs. A face shield is not an acceptable substitute for goggles for eye protection. Adequate eye protection must be worn in addition to the face shield.

Respiratory Protection

Respiratory protection is needed whenever the atmosphere is contaminated with noxious gas fumes or dust, or in case of oxygen deficiency. The correct type of equipment must be chosen for each type of exposure.

Pocket-Type Respirator (Gasfog)*

It is for protection against low concentrations of acid gases and organic vapors including chlorine but excluding HCN. It is for use only where there is no oxygen deficiency.

Canister-Type Gas Mask

These masks are for use only where there is no oxygen deficiency and where the maximum gas concentration encountered is about 2%. They should not be depended upon for exposures longer than about five minutes, which would normally be time enough to escape from the contaminated area or to carry out a quick rescue operation. The canister should be replaced after each such use. When such a mask is used for occasional exposure to very low concentrations of gas, a regular replacement schedule should be set up based on the frequency and severity of exposure.

GMD* canister (green) for ammonia.

GMK* canister (white with green stripes on bottom) equipped with COMFO half-mask face piece for HCN.

*Mine Safety Appliance Company's designations and specifications of capabilities may be found in that Company's publications.

GMA* canister (black) for organic vapors and ozone.

GMC* canister (yellow) for organic vapors and acid gases except HCN.

MCA* canister (red) for all gases including carbon monoxide, singly or in combination. This canister is used where nature of possible gas risk is variable.

Chemox* Oxygen Breathing Apparatus

This type of mask gives complete respiratory protection against all gases and fumes for a period of 45 minutes but affords no protection against poisoning by absorption through the skin.

Eight-Minute Oxygen Demand Masks

Suitable for jobs of short duration or for escape.

Dust Respirators

These are general purpose respirators and should be used for:

Huiscance dust - for example, coal, ashes, cement, sawdust, charcoal, carbon.

Lung-damaging dust - for example, quartz, asbestos, sand.

Toxic dust - for example, arsenic, barium, chromium, copper, lead, manganese.

In addition to the general-purpose respirators, there are some that are designed for specific purposes, such as spray painting in open spaces with organic solvents and thinners.

A respirator, to give adequate protection, must be properly fitted to each individual. Respirators fitted to one person should not be worn by another.

Specific canisters should be selected in advance and made available at the site where they may be needed

*Mine Safety Appliance Company's designations and specifications of capabilities may be found in that Company's publications.

Protection for Hands, Skin and Body

The following equipment is designed to protect the person and his clothing from damage and/or injuries resulting from splashes and spills of chemicals, excessive heat and falling objects. Its use is dependent upon the hazards which exist. However, protection needed should be defined and strict requirements stated.

Aprons and Flame-Resistant Coats

Detailed regulations for use should be established.

Gloves

Asbestos - Used in handling very hot objects. Care must be exercised in their use since asbestos gloves can become hot enough on the outside to inflict severe burns without the knowledge of the wearer.

Leather - Used for protection against cuts when working with glass.

Rubber - Used when handling or working with corrosive chemicals.

Cotton-Canvas - For general light-duty use.

Mitts (Moleskin) - A heavy duty glove for work where wear and tear or heat is encountered.

Special Purpose Gloves - Used in handling organic solvents and chlorinated hydrocarbons.

Safety Shoes

They are entirely suitable for general purpose wear, and their use is highly recommended and in some places obligatory. They prevent physical foot injuries. They may also have low electrical resistance and thereby furnish a path whereby static electrical charges may flow harmlessly to ground. See reference (21) for more details.

Hard Hats

Hard hats must be worn by all employees when work is being done above them and there is no intervening solid floor protection, and in all other designated areas. These hats also protect against bumping into piping or other obstructions.

Protective Skin Creams

Protective skin creams are used to protect the hands and other exposed areas from grime, grease, or paint. Baby oil or an industrial cold cream can be used as skin conditioners. The application of baby oil or equivalent at the end of each day keeps the skin in good condition, especially when the person has been handling solvents which remove the natural oils.

SAFE DESIGN OF EXPERIMENTAL ASSEMBLIES

It is suggested that the following outline be used in planning and installing all laboratory assemblies of various kinds for carrying on research investigations.

1. Think out the problem as to its objective, scope and limitations. Size of operation should generally be held to a minimum, because hazards usually increase with scale of operation.
2. Discuss the problem with other persons who may be familiar with operation and the hazards involved no matter where he may be employed.
3. Decide on location. Factors which may affect the specific location are: need for protection because of toxicity, explosive properties, flammability, or pressure involved; need for standard or special utilities; size of operation; and other work being done in the areas under consideration. Locate the equipment so that egress from the area will be unobstructed.
4. Plan the set-up. Design it as simply as possible to fulfill the objective. Consideration should be given during design to these factors:
 - (a) Hazards involved such as release of toxic, flammable or corrosive materials, etc.
 - (b) Need for equipment such as pressure releases, guards, screens, splash pans, fire-fighting equipment, signs, etc., to protect operators of your unit and personnel and equipment in the area.
 - (c) Accessibility of controls (not obstructed by guards, screens, hot pipes or apparatus).
 - (d) Materials of construction.
 - (e) Adequate supports to avoid vibration, strains on glassware, etc.

5. Assemble the apparatus. Observe the usual precautions in handling glassware. Use proper tools, in good condition, including ladders. Provide supports as required. Protect other workers and apparatus in the area.

6. Review the completed installation with the supervisor in charge of the work. Consider the advisability of having the set-up inspected. Make tests and/or dummy runs, if considered advisable because the set-up is unusual or complicated, or if new principles are involved which would introduce hazards.

7. Familiarize personnel operating the equipment with the set-up and the reasons for the safety precautions involved. Warn persons working in the immediate vicinity about the potential hazards of the operation.

8. Review the installation when changes in scale or method of operation are contemplated to insure that the essentials of safety and simplicity are preserved.

9. Think through the dismantling procedure and make sure all hazardous chemicals are properly disposed of and all pieces of equipment are carefully depressurized.

Glassware Hazards

The misuse of laboratory glassware can result in painful injury. Such injuries can be prevented by careful handling.

Choice of Glass

Hard glass (Pyrex, Vycor, or Kimex) is usually best suited for general laboratory application.

Inspection of Glassware Before Use

Glass strength is directly related to the condition of the glass surface. Glassware that is cracked or severely scratched should not be used.

Other hazards for which glassware should be inspected before use are pinholes, sharp edges, paper-thin areas, badly fitting joints or plugs, and dangerous contamination.

Damaged or defective glassware should be repaired immediately or discarded. The glass blower's advice should be followed if there is any question in this regard. Never ask the glass blower to repair dirty equipment.

Handling Laboratory Glassware

Glass Tubing and Glass Rods

Small-bore tubing and rods up to 20 mm. O.D. should be given a single transverse scratch with a sharp, flat mill file or equivalent cutting device at the point of the desired break. The tubing or rod should be grasped firmly so that the scratch is between the hands and opposite the thumbs. Bend the tubing or rod at the scratch to create tension on the scratched side, and at the same time, pull the hands apart. With glass rod or tubing too short to allow a firm grasp, extend the segment on each side of the scratch with metal or hard plastic tubing. Two cork borers of the proper size will usually serve this purpose.

If over 20 mm. in diameter, or if the tube or rod is connected to a fixed object, thus limiting the pulling possibilities, the glass should be scratched as outlined above, touched with a white-hot piece of glass rod at the center of the scratch and immediately wetted with water. The larger diameter tubes and rods are more conveniently cut by application of a hot-wire technique. Consult a glass blower before attempting use of this method, if possible.

Fire polish or grind the sharp edges of all glassware before use.

Connections to Rubber or Plastics

When glass tubing, rods or thermometers are inserted in holes in stoppers, rubber tubing or plastic tubing, there is danger of the glass breaking to leave sharp jagged edges which may inflict severe cuts. It is often good judgment to wear leather gloves. The following precautions are recommended:

1. DO NOT TRY TO FORCE ANY GLASS TUBE, ROD OR THERMOMETER THROUGH AN OPENING.
2. When inserting any type of glass equipment in cork or rubber stoppers, hold the stopper firmly with thumb and forefinger, keeping the palm of the hand away from the opposite face of the stopper. Firmly grasp the glass as close as possible to the stopper and insert with a series of twists, pressing gently with each twist. The use of a lubricant such as water, glycerol, silicone stopcock grease or powdered graphite is recommended.
3. Where convenient, use the stronger heavy-wall, hard-glass tubing in sizes of 15 mm. or lower, which is now available.

4. In cases where glass equipment is frozen in rubber or plastic and salvage of the equipment is important, cut the material away from the glass.

Ground-Glass Joints, Stopcocks and Glass Stopper.

Ground-glass connections should be clean and lubricated to make them liquid- and vapor-tight and to prevent "freezing". Spring devices are available for holding ground-glass joints together. Stopcocks should be secured with standard stopcock retainers.

Sometimes frozen ground-glass connections can be freed by application of hot water or hot air to the outside surface and gently forcing while wearing gloves. Where permissible, an open flame may be applied to the outside surface. Frozen stopcocks may be freed by means of a mechanical opener. In extreme cases the glass blower should be consulted. When the equipment is not in use, a piece of paper should be inserted between the surfaces of the joint.

Test Tubes, Flasks and Beakers

The limited strength of glass should be kept in mind when corks and stoppers are inserted in the mouths of test tubes and flasks and when heavy beakers and flasks are lifted or supported. Uniform heating to avoid thermal strains and cracking becomes important as beaker or flask size increases above 1 liter; bath or electrical heating is preferable to use of a direct flame.

Physical Explosion Hazards

Physical explosions in the laboratory are usually due to failure of glass vessels under pressure. It is not safe to use glass for operations in which a difference between external and internal pressure may be developed unless adequate precautions are taken against the hazards of flying glass.

Sealed Reagent Bottles

Long-stemmed bottles such as those sometimes used for packaging bromine should be chilled thoroughly, except for the stem, in an ice bath. A scratch is made near the top of the exposed stem, using a sharp file. Generally, a sharp tap will cause the tip to break off. In resealing, the bottle is kept cold as above and the neck heated by means of a hand torch, pulled out, and sealed. This should normally be done by the glass blower.

Containers for Dry Ice

Dry ice or liquins that boil below room temperature should never be placed in a container provided with a tight-fitting closure unless the container is designed to withstand the pressures that will be developed.

Containers stored for extended periods over dry ice tend to absorb considerable carbon dioxide through cork stoppers or around glass or loosely fitting rubber stoppers. When such containers are removed from cold storage and allowed to warm rapidly to room temperature, the carbon dioxide they contain has been known to develop sufficient pressure to burst the container with explosive violence. The stoppers of containers removed from any cold storage should be loosened at once sufficiently to permit release of pressure which might develop during warming.

Vacuum Equipment

The hazards of laboratory operations under vacuum are similar to those of above-atmospheric pressure work, although in general less severe. Accidents in this type of work are most commonly caused by the collapse (implosion) of glass equipment, which may cause injury from flying glass and from hot or corrosive materials contained in the collapsed vessel. Inward leakage of incompatible materials, e.g., of air into hot combustible vapors or of water into concentrated sulfuric acid, may also be a hazard under some conditions. This leakage type of hazard is not, of course, confined to glass apparatus.

Laboratory equipment designed for use under vacuum is usually symmetrical in form with surfaces convex outward. This provides maximum strength against pressure from the outside. Examples of this type of construction are: balloon flasks, vacuum receivers, tubing. When flat surfaces or irregular forms are necessary, e.g., in filter flasks and vacuum desiccators, the needed strength is provided by thickening the walls. Thin-walled vessels with flat surfaces, e.g., Erlenmeyer flasks, beakers, volumetric flasks, French square bottles, are very likely to collapse under vacuum. Large bottles are also subject to collapse even though made of heavy glass. Sealed vacuum units such as Dewar flasks and vacuum-jacketed rectifying columns provide a special case, since they are under vacuum at all times, even when not in use. Regardless of design, glass equipment under vacuum should always be regarded as potentially hazardous. Scratches or flaws in the glassware, mechanical shock or sudden changes in temperature will increase the chance of collapse.

As in all hazardous operations, thought and care should be taken to provide protection against the worst occurrence that can be visualized. The following are some of the means available for such protection:

1. Safety spectacles will protect the eyes against flying glass from directly in front of the operator, but will not provide adequate protection against liquids. Goggles should be worn when working with any eye-irritant or hot liquids under vacuum.
2. Safety shields will protect against an implosion to the extent that they can be placed in direct line between the apparatus and the operator.
3. When the size, shape or location of the apparatus prevents the effective use of shields, other means of protection, such as wrapping with an asbestos blanket, surrounding with wire screening, or coating with plastics, may be used. Portable pieces of vacuum apparatus such as Dewar vessels and vacuum desiccators should always be protected with permanent metal casings.
4. Be sure that the valves leading to the source of vacuum are open before applying heat to an apparatus which is believed to be under vacuum.

It should be kept in mind that the pressure differences obtained with a water pump or a stream aspirator are nearly as great and essentially as hazardous as pressure differences obtained with an oil or mercury vapor pump.

Electrical Hazards

The following specific items are offered as a guide to the responsibilities of the laboratory personnel in avoiding electrical hazards:

1. Inspect all electrical equipment prior to use for damage and chemical or moisture-contamination. If there is any question as to the reliability or safety of the unit, do not put it in operation until it has been checked and approved.
2. New electrical equipment must be inspected by a competent inspector.
3. When electrical equipment is moved to a new location, make sure the circuit provided can carry the additional load.
4. Makeshift connections between non-mating plugs are positively forbidden.

5. Some specialized equipment, for example, oscillographs and certain vacuum tube volt meters, must not be mechanically grounded as is standard on most units in the plant. Where this is the case, the equipment should be so marked and special care exercised in its use.

6. Only approved explosion-proof electrical equipment is permitted in hazardous areas. This should be checked before ordering or installing new equipment. Make sure that all electrical equipment including instruments meets the area requirements. In laboratory hoods or on laboratory benches where flammables are being handled, use caution with open electrical equipment such as stirrer motors and heater thermostats.

7. All cases of electric shock must be reported at once to supervision, and the equipment from which the shock was obtained must be checked and repaired before further use.

8. It is dangerous to permit body contact with any live power circuit because the voltage may be higher than it is supposed to be. Remember that contact with as little as twenty volts may result in loss of muscular control, and there are many fatalities each year through contact with the standard 110-volt household power supply.

9. Glas-Col heating mantles should be used with care. They are not "liquid-proof". When water or other conductive liquid is spilled on a mantle which is connected to a source of current, anyone touching the mantle or associated metal equipment may receive a serious electrical shock. The shock hazard can be minimized as far as associated metal equipment is concerned by fastening the ground clip from the mantle cord to the metal equipment in contact with the mantle. This applies also to metal equipment heated with glass heating tapes. However, there is no way to ground the mantle itself, so if a mantle becomes wet it should be disconnected and not reused until it has dried thoroughly.

10. Static charges may develop through motion of solids, liquids, and gases. It is important that static hazards involved in the handling of flammable materials in experimental work be given careful consideration. Standard antistatic equipment as static dissipating belts, drum fittings with grounding clamps and grounded steam hoses are provided and should be used where needed.

SPECIAL HAZARDS OF LARGER SCALE OPERATIONS

The hazards of larger-scale equipment are principally those of semi-works or pilot-plant installations. The inclusive term semi-works implies facilities which are between the largest laboratory scale (as 5-10 gallon size) and commercial scale equipment. Also, the ten-

embraces operations from a single process step, as practiced in unit operation studies, to a completely integrated pilot-plant installation of sufficient size to demonstrate an over-all process and to develop the necessary information and data for the design of a commercial plant.

Semi-works research carries over from the laboratory most of the hazards inherent in the chemistry of the process, and, in some cases, magnifies them. For example, a rapid exothermic reaction may be carried out on a laboratory scale without any apparent control problem, but when the reaction is scaled up 100 or more times, the removal of large quantities of heat presents a problem for safe and effective operation. Before a new chemical processing operation is carried out on a semi-works scale, the important physical and chemical properties of the materials involved must be known so that the potential operating hazards can be anticipated and equipment and facilities provided to operate safely.

The same engineering standards used in the design and selection of plant-scale equipment should be applied to installations in Semi-Works areas.

Larger-scale research equipment is constructed usually of metal rather than glass used for smaller scale work because of the greater heat conductivity of metals. Since opaque materials are used the physical state of the materials in process cannot be observed. Glass equipment must not be used unless it has been designed specifically for the application. To indicate the conditions existing in a processing system at all times and to give advance warning of approaching hazardous conditions, sight glasses, measuring instruments, control apparatus, relief devices and other "tell-tale" systems must be provided. From a safety viewpoint, reliance on make-shift and untried measuring and control devices must be avoided.

In addition to the foregoing general policies to be followed in the planning and operation of large-scale equipment, the following rules and practices must be observed in programs involving semi-works scale equipment.

1. A comprehensive flow sheet must be prepared as the initial step, showing individual pieces of equipment, piping and valve arrangement, conditions of pressure, temperature and material flows, and elevation of essential pieces of equipment. The flow sheet must be checked by the group leader and supervisor in charge of the project.
2. Detailed plans for connecting semi-works equipment to plant utilities, other than for normal heating and cooling, must be cleared with the plant engineer to insure against some faulty operation affecting a utility service which might result in serious damage to a vital plant facility.

3. Newly fabricated or purchased units, including all safety devices, must be tested for tightness and mechanical defects prior to installation. Also, used equipment must be inspected, serviced and tested as appears necessary to insure safe operation.

4. Detailed operating and safety instructions, including a simple description of the process, concise operating instructions and emergency shut-down procedures, must be prepared before processing activities are started. A clear flow sheet of the installation must accompany the operating instructions, and the main pieces of equipment should be marked to permit a direct reference in the operating directions. All recognized hazards must be listed as a preface to the operating details, and the precautions to be observed must be clearly stated. If special emergency action is indicated, periodic practice drills must be indicated, including the use or application of emergency equipment.

5. Before starting any operation on a semi-works installation, an inspection must be made by a committee to check safety and engineering standards. This inspection will include a meeting preceding the plant inspection to review the flow sheet and operating instructions. The membership of the committee should be selected from different plant groups familiar with the safety standards for large-scale operation. As a general rule, the committee should consist of a representative of the plant safety group, the research supervisor in charge, a representative of the research laboratories and representatives from other appropriate plant groups such as construction, engineering, etc., as deemed necessary.

6. Phantom or dummy runs with pilot-plant installations must be made prior to the initial processing activities to enhance the safety of starting up a new process. These serve as practice runs for training operators and provide a means for checking the over-all mechanical performance and safety of the equipment under conditions simulating regular operations.

7. Regular inspection and maintenance of all apparatus having moving parts must be practiced to prevent accidents resulting from mechanical failure.

8. When the use of a semi-works or pilot-plant assembly on a given job is terminated, the equipment must be thoroughly cleaned and checked throughout so that it can be safely dismantled or used on another job. Any damaged or defective equipment must be immediately repaired or scrapped.

9. No chemical processing operations are permitted on a semi-works scale in which known or suspected explosive hazards exist without (a) adequate controls to minimize the possibility of an explosion and (b) barricading to protect personnel from injury.

10. Deviation of process behavior must be treated as a grave warning of danger. Temperature either higher or lower than expected means a very critical condition exists DO SOMETHING!

Occasionally an operation is conducted in a semi-works area that more closely borders on laboratory scale operation than normal semi-works operation. Under this condition, the person in charge of the job should contact the proper research supervisor and agree on the safety regulations listed above that may be modified or eliminated on the particular operation. In case any major changes are subsequently made in the program or equipment, it is the responsibility of the person in charge of the job to review them in detail with the research supervisor.

FIRE PREVENTION

Fires account for a tremendous yearly toll of injuries, loss of life and destruction of property. They are a particularly dangerous hazard in chemical plants and laboratories, so that every possible precaution must be taken to prevent their occurrence. Precautions may be generalized as (1) control of flames, sparks and other fire initiators, (2) safe handling and storage of flammables and combustibles, and (3) good housekeeping.

Control of Fire Initiators

Observe all no-smoking rules as posted. Smoking is permitted in offices, conference rooms and lunch rooms and is usually permitted at the desk areas in most laboratories, but is not permissible in the bench or working zones of laboratories. Smoking at desks in laboratories, where this is ordinarily permissible, should be restricted by the occupants whenever conditions dictate, e.g., if appreciable amounts of flammable solvents are being used near the desks. Matches, cigarette butts and pipe ashes should always be placed in ash trays and not thrown into waste baskets or other containers.

Care should be taken to keep flames and sparks away from the vapors of flammable solvents or gases and combustible dusts. In this connection it should be remembered that highly flammable materials such as carbon bisulfide vapors will ignite on contact with hot steam pipes and hot plates. Only explosion proof motors, switches, lighting fixtures, and electrical devices should be used in the presence of flammable vapors. Volatile flammables should never be placed in electrically heated ovens. Refrigerators for storing flammable materials must always be rendered explosion-proof by removing all sources of ignition.

Storage and use of spontaneously flammable materials, such as yellow phosphorus, should be carefully supervised and the quantity of such materials handled or stored should be kept to a minimum. Oily rags and papers that may ignite spontaneously should be placed in closed waste cans that are emptied daily.

Care must be taken to avoid ignition of vapors or dusts by sparks from static electricity, the collision of metal objects, and grinding operations. Spark-proof, plastic-coated tools are a prerequisite in flammable atmospheres.

Safe Handling of Flammables

All combustible liquids having a flash point of 80°F or below by the open-cup test, or having a boiling point of 300°F (150°C) or below, are to be considered flammable. In order to reduce the fire and explosion hazard associated with such liquids to a minimum, the following limits have been established with regard to storage and handling in the laboratory.

1. The maximum volume of flammable liquid per laboratory chemist shall be 6 quarts exclusive of waste solvents.

2. The maximum volume of flammable waste solvent per laboratory chemist shall be 1 gallon. It must be stored in a safety can.

3. The maximum capacity glass bottle for storing flammable liquids shall be 1 quart.

4. The maximum capacity metal safety can or polyethylene bottle for storing flammable liquids shall be 1 gallon. No other type of container having a capacity greater than 1 quart shall be used for storing flammable liquids in the laboratory.

It is recognized that for purposes of economy certain laboratory jobs will require use of more than the above maximum amounts of flammable liquids. Exceptions to these limits must have the approval of the research supervisor, and where use of larger amounts of flammable liquids is permitted, special precautions must be observed. Examples of special precautions are prohibition of smoking anywhere in the laboratory, provision of extra fire extinguishers, and use of metal containers under or around large glass containers.

Flammable liquids that are not in current use or that exceed the above limits in quantity should be stored in the areas especially equipped for this purpose.

Steam or hot water should be employed wherever possible for heating flammable liquids to avoid ignition in case of spillage. When heating flammables in glass by flame or electricity, a metal catch pan of sufficient size to hold the contents of the container should be placed underneath.

Waste flammables in liquid form should preferably be collected in a properly labeled safety can provided for such use. Flammable liquids immiscible with water should never be run into a sink or sewer. Those that are miscible with water may be disposed of in a sink if first mixed with enough water to make them non-flammable.

Housekeeping

Good housekeeping is an excellent fire precaution. Combustible wastes, paper, cardboard, wood, and other combustible litter should not be allowed to accumulate.

TOXICITY AND SKIN HAZARDS

All chemicals should be regarded as toxic unless widespread usage and toxicity studies have proved them harmless under the conditions of handling. This concept is necessitated by the fact that over one-half million chemicals are described in the literature, and only a few of these have been studied sufficiently to define their toxic properties.

There are three main channels through which poisonous materials can accidentally enter the human system:

1. Breathing into the respiratory tract in the form of dusts, fumes, vapor, mist or gases. (Discussed fully in the next section).
2. Swallowing with food, saliva or water.
3. Absorption through the skin, or entrance through breaks in the skin.

Results of poisoning by any of these routes may be acute or chronic. In acute poisoning the results are usually readily apparent, in chronic poisoning the effects may not show up for years.

Care should be taken that toxic materials are not accidentally ingested through the mouth.

Skin afflictions account for the largest number of occupational-disease cases of any group of causes. Differences in individual susceptibilities to exposures of this type make it very difficult to set up standards for the safe handling of any chemical. The hands and face should be washed frequently when exposed to chemical dusts or solutions. Since many chemicals are readily absorbed through the skin, long contact even with those chemicals which are supposedly harmless should be avoided. A change in solvent may nullify the protective action of skin oils and

make even a short exposure harmful. For example, a short exposure to an aqueous solution may be harmless while the same exposure to the same agent dissolved in methanol or trichloroethylene may produce a major lesion. Protective items such as gloves, aprons, face shields, protective creams, etc., should be worn to prevent contact with the body. Any sign of skin irritation should be immediately reported to the Medical Officer.

In working with chemicals of known hazardous type, it is wise to consult with someone familiar with the materials or classes of materials involved. Hazards relating to some special classes of chemicals will be discussed in later sections of this manual. For additional general information, reference material in the Library should be consulted. Pertinent sources of information are references (2), (15), (16), (17), and (18).

Statements in these and other references on toxic limits and precautionary procedures are suitable only for general or approximate guidance. When such data are of prime importance to the usage of handling of specific chemicals, confirmatory opinions should be obtained. Omission of chemicals from these references should not be considered as indication of lack of toxicity.

Hazards of Toxic Gases

The contamination of air in working areas by any vapor, gas or dust should be regarded as dangerous, even if concentrations are low. In most cases the degree of contamination in air supposed to be safe for prolonged or repeated exposure is uncertain. Inhalation of some gases will, in a matter of seconds, cause serious injury or death, while in the case of others, reaction may develop gradually over a period of years, resulting finally in irreparable damage. Even a mild anaesthesia or unsuspected intoxication may impair judgment enough to cause an accident.

Even though an unpleasant odor may not be evidence of the presence of toxic materials, it may be distracting enough to be a contributory factor in a seemingly unrelated accident. If any odors are noticed, their source should always be located quickly and the situation corrected immediately. The help of supervision should be enlisted to accomplish this end, if necessary.

From the standpoint of respiration, noxious materials may be classed as:

1. Irritants. Irritants may affect any part of the respiratory

system, the nose, throat, lower air passages or lungs. Examples are:

Ammonia	Acetic acid
Halogen acids	Acetic anhydride
Sulfuric acid	Sulfur halides
Formic acid	Sulfuryl chloride
Thionyl halides	Nitrogen oxides (except nitrous)
Sulfur dioxide	Phosgene
Chlorine	Acrolein
Bromine	Dimethyl sulfate
Arsenic compounds	Active-halogen organic compounds
Phosphorus chlorides	Hydrogen sulfide
Ozone	Boron hydrides

2. Asphyxiants. These agents interfere with the supply of oxygen to the body tissues. They may be (a) gases which merely displace the free oxygen in the atmosphere, (b) gases which act on the nervous system to paralyze the respiratory center and (c) gases which change the blood or body tissues chemically so that the oxygen reaching the lungs is not used. Examples are:

- a. Any gas other than oxygen
- b. Hydrogen sulfide
- c. Carbon monoxide

Volatile cyanides such as

Hydrogen cyanide

Cyanogen

Cyanogen chloride

Acetonitrile

Acrylonitrile

3. Systemic Poisons. Such agents are absorbed through the respiratory system, enter the blood stream, and affect a site other than the point of contact.

Examples are:

Benzene	Cycloparaffins
Toluene	Organic nitrocompounds
Styrene	Carbon disulfide
Butane	Boron hydrides
Alcohols	Mercury and its compounds
Aldehydes	Arsenic and its compounds
Ketones	Selenium and its compounds
Ketene	Antimony and its compounds
Ethers	Lead and its compounds
Halogenated hydrocarbons	Metal carbonyls
Aromatic amines	Phosphorus
Esters	

Preventive Safety Measures

While toxic gases vary widely in specific physiological effects, the basic essentials of avoiding trouble are the same for all gases; namely,

1. Supply adequate amounts of fresh air to working areas.
2. Avoid contamination of air in working areas. Do experiments which involve toxic gases in well-ventilated hoods which exhaust so that fumes cannot enter working areas. Check efficiency of hoods frequently.
3. Know how to use gas masks and other breathing apparatus and use them whenever there is a chance of inhaling toxic gases.
4. Know the limitations of filter-type masks.
5. Give alarm if toxic gases are released into any working area, and take measures to correct the situation.
6. If the toxic action is rapid, antidotes should be at hand before any experimental work is begun.

First Aid for Victims of Gassing

Inhaled gas is usually instantly absorbed by the blood, which circulates a moment later to the brain, making injury possible within seconds (anaesthesia, nerve paralysis, cessation of breathing). Man has limited control over his breathing. He can hold his breath only $\frac{1}{2}$ to 1 minute after inhaling, and considerably less after exhaling. Hence, even if warned, one may be unable to avoid breathing a poison. If the poison causes breathing to stop, the victim will probably die from lack of oxygen even though the poison in the air were to be immediately removed.

Indeed the life of a gassed victim is often in the hands of the first one to arrive, and the outcome may depend more upon his knowledge of proper procedure than upon the doctor who may later treat the patient in a hospital or first aid station. Therefore, the basic principles of first aid treatment should be understood by all fellow workers.

EXPLOSIVE OR VIOLENT REACTIONS

Potential reaction violence or explosion can be forecast. Experimenting can be safe even though an explosion does occur. Therefore, personal injury from explosive or violent reactions must be attributed to human failure in foresight and forethought.

Forecasting Violence or Explosion Danger

High energy substances, as a class, are capable of exothermic reaction.

Exothermal reactions can self-accelerate; reaction rate goes up with temperature, and temperature goes up as reaction proceeds. This can cause uncontrollable reaction violence. Also, a reaction which makes gaseous products can become violent if provision is not made to disengage and vent the gaseous products. Explosive reactions are exceptionally violent reactions characterized by a nearly instantaneous release of heat or gas or both, occurring throughout a quantity of material.

If a compound or mixture can decompose to form gaseous products, and if this decomposition is quite exothermal, then the material is a potential explosive. Any of these explosive materials may be sensitive, such as a perchlorate ester, or relatively insensitive, such as pure hydrogen peroxide. Supposed low sensitivity cannot be relied on in laboratory work, except to a very limited extent.

Calculation of heats of reaction is helpful in forecasting danger. All possible reactions should be considered, not just the desired reaction. This is not as hard as it sounds because the products are usually simple, such as H_2O , CO_2 , CO , N_2 , C , Cu , etc. When no data are available they can usually be had simply by having heats of combustion measured, or they can be approximated from bond energies. If unfamiliar with these calculations, you can have them made by others. These calculations are to be regarded as aids in forecasting explosion hazards. They do not cover all cases, notably some of the organic peroxides and polymerizable organic compounds.

Chemical structure can help in recognition of potential explosive organic compounds. The following groupings tend to confer explosive

character: $-ONO_2$, $-NO_2$, $-NO$, $=N-NO_2$, $-N=N-$, $-O-O-$, $-N_2$, $-C=C-$. Two or more such groups in a molecule usually make the compound potentially much more dangerous. Compounds containing enough oxygen to oxidize most of the oxidizable elements are likely to be very dangerous.

Experiences of yourself and others, together with analogous reasoning, are helpful in recognizing dangerous materials. Lists of hazardous compounds are worth memorizing, particularly those items which you would not expect to be dangerous in the light of your own chemical background.

Even when reactants and main products are safe, we should not forget the possibilities of explosive intermediates, by-products, or residues. For example, peroxide formation can occur in ethers such as diethyl ether and tetrahydrofuran.

Many dangerous reactions are described without a word of caution in published literature. Hence, literature precedent is a poor basis for disregarding any known indication of hazard. On the other hand, library searches can help find hazards of specific compounds. Additional information on forecasting explosion hazards is given by Tomlinson and Audrieth, reference (19).

Recommended Procedures for Potentially Explosive Reactions

Plans to run any reaction that may be explosive or will yield explosive products or by-products, should be thoroughly reviewed with supervision. The following recommendations apply:

1. The scale of reaction should be limited to the smallest practicable quantity, in any case not more than one-tenth mol* of potentially explosive material. Micro-analytical techniques can help in drawing valid conclusions from this small-scale work.
2. All personnel within the area should be completely shielded from direct line missiles. For the recommended scale, a minimum of $\frac{1}{4}$ in. standard safety glass (not tempered glass), $\frac{1}{8}$ in. "Lucite", or $1/16$ in. mild steel is adequate. There should be a minimum spacing of ten inches between the shield and the reactor to prevent high-velocity fragmentation of the shield.

*The first experiment should be limited to one-hundredth mol.

3. Conduct all operations by remote control. There is no point in shielding if you reach around the shield. Before starting a reaction, distillation, or other operation, think through the whole procedure and make adequate preparation for safe handling of potentially explosive products or residues.

4. Dilution of an explosive material with enough solvent can make it entirely non-explosive. However, the possibility should be borne in mind of dangerous concentration of the material by fractionation, separation of liquid phases, etc.

5. Cooling with Dry ice or liquid nitrogen is helpful in manipulating unstable explosive materials. There are compounds, however, which may still explode when cooled thus. Liquid air is not recommended because of the danger of scattering liquid enriched with oxygen in case of explosion.

6. Gas mixtures, even though used in the non-flammable range, should be regarded as explosive materials if they could possibly become so by incorrect mixing. Hydrogen with air is an example of such a mixture.

7. Successful completion of small-scale experiments without explosion must never be taken to prove absence of hazard.

Recommended Procedures for Potentially Violent Reactions

Many reactions with large heat or gas-release are potentially violent but not explosive because the materials react very rapidly during mixing, so that dangerous quantities of unreacted mixture do not build up. For such reactions, the following recommendations apply:

1. Unless the specific reaction is well known, the first run should be on a very small scale, even though others elsewhere have made larger runs. Once the reaction is known to proceed promptly and smoothly, consideration may be given to larger scale reaction.

2. Any indication of an induction period, or delayed reaction, should be taken as a danger signal, putting the reaction of this type in the class of potential extreme violence or even explosiveness.

3. All measures for reaction control should be simple, rugged and sure to work. These control measures include gradual addition of reactants and effective stirring, heat dissipation, gas venting, and temperature indication. If possible, some means should be available for quenching the reaction in case of need.

4. You and your neighbors should be protected by shielding. Personal protective equipment such as goggles and gloves should also be used in the vicinity of the experiment. Precautions should be taken against fire in case the reaction gets out of control.

PEROXIDIZABLE SOLVENTS

Peroxides that form in common laboratory solvents have been one of the most frequent causes of laboratory explosions. Such explosions occur most frequently during a distillation or after a distillation has been completed and the equipment is being dismantled. Peroxidizable solvents should not be used in work with explosives. If their use cannot be avoided concentration of peroxides in the explosive must be prevented as they may initiate detonation. Explosions have been known to occur during opening of bottles in which ethers had been stored.

The following compounds are examples of common laboratory solvents that peroxidize easily:

<u>Ethers</u>	<u>Hydrocarbons</u>
Dioxane	Cyclohexene
Tetrahydrofuran	Tetrahydronaphthalene (tetralin)
Diethyl ether	Decahydronaphthalene (decalin)
Diisopropyl ether	Branched-chain saturated hydro-
Ethylene glycol dimethyl ether	carbons
Diethylene glycol dimethyl ether	Alkyl-substituted cycloaliphatics

The rate of formation of peroxides is increased by exposure to light, heat, and air. It can be very rapid. For example, a detectable amount of peroxide has been noted in cyclohexene within one hour after distillation from sodium and storage in a glass-stoppered bottle.

Precautions

1. Easily peroxidizable solvents should be protected from light, heat and air during storage. Blanketing with nitrogen and use of well-closed containers are recommended.
2. Containers of peroxidizable materials should be marked with adherent tape imprinted with "Warning-May Contain Explosive Peroxides".
3. Such containers should be dated when first opened (a) after receipt from the vendor or (b) after removal of peroxides and storage under nitrogen.

4. Peroxidizable solvents that have been exposed to air should be kept for a maximum of six months. Then they should be discarded or else treated to remove peroxides.

5. Before a peroxidizable solvent is used in an operation in which any contained peroxides would be concentrated, the solvent should be tested for peroxide content. Test methods are described below. If peroxides are present, they should be removed. Removal methods are described below.

6. During distillation of a peroxidizable solvent, air should not be allowed to come in contact with the hot solvent.

7. A peroxidizable solvent that is being concentrated and the residues obtained should be treated as explosive materials as outlined in the above section on Explosive or Violent Reactions.

Detection of Peroxides

1. Dissolve a sample in glacial acetic acid. Add a few drops of a 10-15% solution of sodium iodide in acetone. If a color develops, peroxides are present. A yellow color indicates a low concentration, and brown a high concentration of peroxide in the sample.

2. Add some of the material to be tested to an acidified 5-10% aqueous solution of sodium or potassium iodide. Agitate vigorously if the material does not dissolve. Add starch solution to the aqueous phase. If a blue color develops, peroxides are present. If the peroxide concentration is high, a yellow color may develop before the starch is added.

Removal of Peroxides

There are several established laboratory procedures for removing peroxides from solvents. No matter which is used, the treated solvent should always be tested to check the effectiveness of the treatment. The following are representative.

1. Peroxides can be removed conveniently by passing the solvent through a short column of ordinary activated alumina. This method is effective for both water-insoluble solvents and water-soluble solvents (except for lower alcohols). It has the advantage that no water is introduced into the solvent, and small amounts of water that may be present are removed. When not even traces of peroxide can be tolerated, it is convenient to have the solvent flow directly into the reaction vessel from the alumina column. For results obtainable with this procedure see reference (20).

Care should be used in disposing of the activated alumina after this operation. Experiments with peroxidized cyclohexene and dioxane indicate that at least these peroxides are decomposed on the alumina rather than simply adsorbed. To be on the safe side it is recommended that alumina that has been used for peroxide removal be flushed with or dumped into a dilute acid solution of potassium iodide or ferrous sulfate.

2. Peroxide impurities in water-insoluble solvents (ether, hydrocarbons, etc.) are easily removed by shaking with a concentrated solution of a ferrous salt. A frequently used ferrous salt solution is prepared either from 60 g. of ferrous sulfate, 6 ml. of concentrated sulfuric acid, and 110 ml. of water or from 100 g. of ferrous sulfate, 42 ml. of concentrated hydrochloric acid, and 85 ml. of water. With some ethers, traces of aldehydes are produced by this treatment. If ether of a high degree of purity is required, it should be further shaken with 0.5% potassium permanganate solution, then with 5% sodium hydroxide solution and finally with water.

3. One of the oldest methods of peroxide removal involves refluxing the peroxide-containing solvent over metallic sodium, followed by direct distillation. Recently, sodium hydride and lithium aluminum hydride have become popular for this use. Peroxide impurities are safely reduced to alcohols which remain behind as insoluble alcoholates during distillation. This procedure can be used generally for hydrocarbons and ethers; remember, however, that a serious explosion can result when halogen-containing solvents, such as carbon tetrachloride, chloroform, "Perclene", "Triclene", etc., are heated with strong reducing agents such as free metals or their hydrides. Obviously, organic reagents such as alcohols, phenols, acids, etc., which contain acidic hydrogen atoms that react with sodium, cannot be purified by this method.

OXIDIZING AGENTS

Hazards in Handling

Oxidizing agents are, by their very nature, hazardous compounds with respect to explosions, fires and burns. Some are poisons and allergens as well. Many of the commonly employed oxidizing agents are classified below according to their primary hazards. This list is not necessarily complete.

Since perchloric acid and perchlorates are especially dangerous because of their sensitivity and tremendous potential destructive power, special permission from supervision must be secured before working with them.

Nitrates, chlorates and other compounds of oxidizing acids should be handled with care whenever mixed with reducing agent, and combustible material. Systems containing an oxidizing acid or salt and organic matter constitute potential explosives. Mixtures containing salts of oxidizing acids are particularly dangerous in the anhydrous state and when subjected

to heat and strong acids. Practical examples of this are common laboratory cleaning solutions and nitrating mixtures. While most of these acids and salts are not dangerous alone, some of the salts are explosive by themselves.

In respect to the explosion, fire and burn hazards, similar considerations apply to the volatile oxidizing agents. In general, high temperatures and high concentrations are to be avoided whenever possible, and any spilled oxidizing agent should be cleaned up promptly.

The better known volatile oxidizing agents all have strong physiological effects. Every one but oxygen is a poison, and when inhaled the fumes may be lethal.

REAGENTS WHICH CAUSE FIRES, EXPLOSIONS AND BURNS

Oxidizing Acids and Their Salts. Iodates, periodates, bromates, hydrochlorites, chlorites, chlorates, perchlorates, nitrites, nitrates, permanganates and chromates; especially salts with reducing and catalytic ions.

Volatile Reagents. Ozone, oxygen, halogens, internalogen compounds, and compounds with nitrogen-halogen, nitrogen-oxygen, and oxygen-halogen bonds.

Solid Reagents Higher-valence compounds of selenium, tellurium, mercury, thallium, lead, arsenic and vanadium.

CHLOROHYDROCARBONS

Flammability

The low flammability of the chlorohydrocarbons as a group is one of the principal reasons for their wide commercial use. The members of the group vary somewhat in flammability as indicated below:

Methyl Chloride - moderately flammable with moderate explosion hazard.

Methylene Chloride - practically non-flammable at ordinary temperatures.

Trichloroethylene - non-flammable at ordinary temperatures.

Carbon Tetrachloride, Perchloroethylene - non-flammable.

Chloroform, Methylene Chloride, and Trichloroethylene - form weakly combustible mixtures at high temperatures with high concentrations of solvent vapor in air.

Toxicity

The toxicity of the chlorohydrocarbons is the principal hazard in their use. A good general rule is that human beings should not be exposed to an atmosphere in which the odor of chlorohydrocarbon is detectable. However, the members of the group vary considerably in toxicity and for this reason attempts have been made to establish maximum concentration limits in air for the individual chlorohydrocarbons. For example, the American Conference of Governmental Industrial Hygienists has set up a list of values called "threshold limit values" which are defined as the maximum concentrations in air to which an individual may be subjected over a long period of time without experiencing undue discomfort. These values are given below for some of the chlorohydrocarbons in comparison with some other solvents commonly used in the laboratory.

Threshold Limit Values (April 1960)

	<u>ppm (vol.)</u>
Methyl Chloroform	500
Methylene Chloride	500
Trichloroethylene	200
Perchloroethylene	200
Ethylene Dichloride	100
Methyl Chloride	100
Propylene Dichloride	75
Chloroform	50
Carbon Tetrachloride	25
Tetrachloroethane	5
Pentachloroethane	5
Ethyl Alcohol	1000
Acetone	1000
n-Hexane	500
iso-Propyl Alcohol	400
Methyl Alcohol	200
Toluene	200
Dioxane	100
Ethyl Acrylate	25
Benzene	25

Maximum concentration values have also been established by State health authorities and these may vary for some compounds from two to tenfold.

The first evidence of the physiological action of the chlorohydrocarbons is a narcotic effect. Symptoms of excessive exposure include headache, undue fatigue, or nausea. Some of the solvents are rapidly eliminated from the system on access to fresh air, with no evidence of permanent effects on body organs. Others, on repeated exposure, may

produce delayed or cumulative physiological effects, such as liver damage. Carbon tetrachloride is reported to have this effect, even in low concentrations, and some others may also.

Particular attention is called to the low allowable concentrations for tetrachloroethane and pentachloroethane. The maximum values for these compounds are lower than for hydrogen sulfide or hydrogen cyanide.

Trichloroethylene-Dry Ice freezing mixture is frequently used in the laboratory. The trichloroethylene should not be allowed to stand in an open container between uses.

Contact of the skin with chlorohydrocarbons, both liquid and vapor, should be avoided. Absorption through the pores may produce the same physiological effects as inhalation. Removal of natural oils from the skin may cause irritation. Contact of vapors with the eyes should be avoided because of the sensitiveness of these organs.

Stability

Under ordinary use conditions, there are no hazards in the handling of the commercial chlorohydrocarbons due to instability. On exposure to high temperatures (e.g., open flames or open electric heaters), the chlorohydrocarbons may decompose to form toxic and corrosive products.

Reactivity

In the presence of sodium, caustic, or caustic solutions, 1,2-dichloroethylene may form monochloroacetylene; trichloroethylene may form dichloroacetylene; and tetrachlorethane may give either of the chloro-acetylenes. Since the chloroacetylenes are highly explosive, contact of caustic with the above chlorohydrocarbons should be avoided except under carefully controlled experimental conditions.

OTHER COMMON CHEMICALS

While the handling hazards of some of the more dangerous chemicals frequently used in our laboratories have already been described, there are many others which present various types of hazards when not handled in the proper manner. It is beyond the scope of this manual to include all of these chemicals, but a few of the more common materials have been selected for discussion. For hazards encountered in handling chemicals not contained herein, reference material in the library and Safety Group should be consulted. See references (2), (21), (22), (23), (24), and (25).

Acids

The mineral acids are very corrosive and capable of producing serious injury or death if handled carelessly. These precautionary measures are required to be followed when these materials are handled.

1. Wear goggles when pouring acids.
2. Avoid contact with skin. If spilled on skin, wash immediately with copious amounts of water. If there is any evident burn from the acid, report to the doctor immediately.
3. Spillage on floor or bench should be cleaned up immediately by flushing with water or dilute sodium carbonate or bicarbonate.
4. Do not use combustibles such as cloth, sawdust, or other organic materials to mop such spills.
5. Always pour concentrated acids such as sulfuric acid into water and never vice versa. Use good agitation.
6. Avoid inhaling acid fumes.

Alkalies

1. In handling alkalies in either solid or solution form, avoid contact with skin or eyes. Goggles should be worn. If the skin or eyes should be affected by alkalies, wash the areas immediately with large amounts of water and report to the doctor.
2. In dissolving solid alkalies, use cold water and wear necessary protective equipment. In making solutions, always add flake or granular forms of alkalies slowly in small portions to avoid boiling and spattering.
3. Spillages of these materials should be flushed away quickly and never left unattended. If the material is a solid, it can be shoveled away and then dilute acetic acid used to neutralize any remaining traces of the material.
4. Avoid breathing of ammonia vapor. If it is necessary to work in area with high concentration of ammonia, wear a Chemox or 8-minute sling mask that covers the eyes.

Mercury

1. Mercury and its compounds should be stored in a cool, well-ventilated place away from areas of acute fire hazard. Containers should be kept closed and plainly labeled.

2. Mercury or its compounds should never be heated in the open, but only under a fume hood.

3. Spills of mercury should be cleaned up immediately. If this is not possible, wet the area with water or sprinkle calcium sulfide liberally onto area until spillage can be cleaned up.

4. Droplets of mercury can be picked up readily using a small steel pipe or glass pipette connected to a suction flask by small bore rubber tubing.

Dry Ice

Dry Ice is a proprietary name for solid carbon dioxide. At ordinary temperatures it will turn into gaseous carbon dioxide. The latter, in high concentrations, paralyzes the respiratory center and causes asphyxiation.

1. Wear dry cotton gloves when handling Dry Ice and do not allow it to come in contact with any part of the body because of danger of frost-bite.

2. When breaking large pieces of Dry Ice with a mallet, wear goggles, and use extreme care that flying pieces do not endanger others in the area.

3. Never store Dry Ice in gas-tight containers.

4. When preparing mixtures of Dry Ice and trichloroethylene or other liquids, add the Dry Ice slowly to control rate of gas evolution and avoid spattering. Wear goggles.

Ethyl Ether

The greatest hazard in the handling of ethyl ether is that of fire and explosion. It is a highly flammable liquid with a flash point of -45°C and the very wide explosive range of 1.85% to 36.5% by volume in air. Although ether is not a very poisonous substance, it can produce anaesthesia, narcosis, and intoxication resembling that produced by alcohol. If ether containing ethyl peroxide is distilled in such a manner as to concentrate the peroxide, it may become explosive.

1. Preparations containing ether should be heated or distilled only over a steam bath or a hot water bath without an exposed heating element. This operation should be carried out under a hood.

2. Materials containing ether should not be placed in electrically heated ovens.

3. Before ether is distilled it should be tested for peroxides. If peroxides are present, they should be removed. See section above on Peroxidizable Solvents.

4. Non-flammable solvents such as methylene chloride should be used in place of ethyl ether for extraction if at all possible.

HAZARDOUS MIXTURES

The possibility that a hazardous mixture may be used or formed in carrying out a chemical reaction should never be overlooked. The rate of reaction, the possible catalytic effect of structural materials, the heat-transfer capacity of the equipment, the stability of the products, and possible by-products, the toxicity and flammability of the off-gases, etc., are important considerations. Previous sections in this manual, as well as the tables below, should be consulted and memories refreshed for furnishing background information on incompatible chemicals before doing work involving a new chemical reaction.

Hazardous mixtures may also result during chemical storage. Care must be taken to prevent the mixing of strong acids and alkalies, sodium and water, carbon disulfide and nitric acid, etc. These could occur by spills, fires, or explosions near stored chemicals which might lead to other fires and explosions of a serious nature.

The problem of waste disposal in the laboratory should also be carefully considered. Organic residues should not be placed indiscriminately in a waste can without sufficient deactivation of the material and a knowledge of the contents of the waste can.

Care must be taken to use the right type of extinguisher for laboratory fire to prevent secondary reactions. Thus carbon dioxide extinguishers should not be used on sodium or magnesium fires.

The following tabulation gives a great many known hazardous combinations of chemicals. Necessarily, no list of this sort can be complete, and it should therefore be considered primarily educational.

1. ACETYLENE and chlorine (or bromine, fluorine) (explosive reactions).

2. ACETYLENE and air (explosive range from 2.5 to 82% C₂H₂ by volume).

3. ACETYLENE and metals which form unstable acetylides, such as copper, silver or mercury.
4. ALCOHOL and nitric acid (rapid oxidation; heat of reaction).
5. ALCOHOL and active chlorine (or hypochlorites) (alkyl hypochlorites form which are very unstable).
6. ALCOHOL, silver salts, and nitric acid (explosive products form).
7. AMINES or AMMONIA plus oxyanions (perchlorate, nitrate, chlorite, chlorate).
8. AMMONIA and nitrous oxide (an explosive mixture).
9. AMMONIA and mercury (mercuri-ammonium oxide formation).
10. AMMONIA or ammonium salts and halogens (violently explosive compound).
11. AMMONIA and silver or silver salts (Ag_3N or Ag_2NH formation).
12. AMMONIA and calcium hypochlorite.
13. AMMONIA and hydrogen fluoride.
14. AMMONIUM nitrate with acids, metal powders, flammable liquids, chlorates, nitrates, sulfur, finely divided organics or combustibles.
15. AMMONIUM PERCHLORATE and carbon (exothermic decomposition).
16. ANILINE and nitric acid, hydrogen peroxide.
17. AZO compounds plus organic reactants or impurities.
18. CALCIUM METAL and sodium hydroxide (detonation).
19. CALCIUM CARBIDE and water (see also acetylene).
20. CALCIUM OXIDE and water.
21. CARBON-ACTIVATED and calcium hypochlorite.
22. CHARCOAL and sulfur, sodium nitrate-Black Powder.
23. CARBON TETRACHLORIDE and electric arc (phosgene in presence of air).

24. CHLORATES, PERCHLORATES, and ammonium salts, acids, metal powders, sulfur, finely divided organics or combustibles (violent oxidation).
25. CHLORINE and ammonia, acetylene, butadiene, butane and other petroleum gases, hydrogen, sodium carbide, turpentine, benzene and finely divided metals.
26. CHLORINE DIOXIDE and ammonia, methane, phosphine, hydrogen sulfide.
27. CHROMIC ACID and acetic acid, naphthalene, camphor, glycerine, turpentine, alcohol, and other flammable liquids (violent reaction).
28. CYANIDES and acids or acid salts (HCN formation).
29. CYANIDE SOLUTIONS and chlorine gas (HCN, C_2N_2 , $CNCI$ formation).
30. CYANIDES and concentrated formaldehyde (a cyanhydrin forms which may polymerize with violence).
31. CYANIDES and nitric acid (explosive reaction).
32. FURFURAL (and derivatives) and strong acids (polymer formation).
33. FORMALDEHYDE and nitric acid (violent oxidation).
34. Gas evolving mixtures in closed containers (pressure ruptures).
35. HYDRAZINE and ferric oxide (ignite at 23°C).
36. HYDROGEN and chlorine, vapor phase (violent reaction).
37. HYDROGEN and air or oxygen mixtures (explosive if in contact with sparks or flames).
38. HYDROGEN PEROXIDE and lead, copper, iron, most metals or their salts (particularly thiocyanate), any flammable liquid, combustible materials, aniline, nitromethane.
39. HYDROFLUORIC ACID and ammonia, aqueous or anhydrous.
40. HYDROGEN SULFIDE and fuming nitric acid, oxidizing gases.
41. HYDROCARBONS and fluorine, chlorine, bromine, chromic acid.

42. IODINE and acetylene, ammonia.
43. KETONES plus hydrogen peroxide and nitric acid (formation of di- and tricycloketone peroxides)
44. MALEIC ANHYDRIDE and a base with heat (explosive formation of CO_2).
45. MOLTEN CYANIDES and oxidizing agents (explosion hazard).
46. MERCURY and lead or aluminum metals (alloy formation).
47. MERCURY and acetylene, fulminic acid, ammonia.
48. MERCURIC NITRATE and hydrocarbon oils (violent reaction with unsaturates).
49. NITRIC ACID (conc.) and acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, nitratable substances.
50. NITROPARAFFINS and inorganic bases.
51. ORGANIC CHLORIDES and peroxygen compounds.
52. ORGANIC CHLORIDES and metals - aluminum powder, iron (particularly in presence of dimethylformamide, dimethylacetamide) may be explosive.
53. OXYGEN and oils, grease, hydrogen, flammable liquids, solids or gases (explosion hazard).
54. PERCHLORIC ACID and acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease, oils.
55. PEROXIDES, ORGANIC and acids (avoid friction).
56. PHOSPHOROUS (WHITE) and air, oxygen
57. POTASSIUM metal and air (K_2O_4 formation).
58. POTASSIUM TETRAOXIDE and organic or combustible material (fire hazard).
59. POTASSIUMpermanganate and glycerine, ethylene glycol, benzaldehyde, sulfuric acid.

60. SILVER and acetylene, oxalic acid, tartaric acid, fulminic acid, ammonium compounds.
61. SODAMIDE and moisture plus air (explosive compound forms).
62. SODIUM (and other alkaline and alkaline earth metals) and carbon dioxide, carbon tetrachloride and other chlorinated hydrocarbons, water.
63. SODIUM and SODIUM PEROXIDE (violent reactivity).
64. SODIUM HYDRIDE and air or water (hydrogen hazard).
65. SODIUM MONOXIDE and water (fire hazard and very caustic).
66. SODIUM MONOXIDE or sodium hydroxide and chlorinated hydrocarbons (possibility of chloroacetylenes forming).
67. SODIUM MONOXIDE and solid CO₂ (violent exothermic reaction).
68. SODIUM NITRATE and ammonium nitrate or other ammonium salts.
69. SODIUM PEROXIDE and any oxidizable substance, such as ethanol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, chlorinated hydrocarbons, glycerine, ethyl acetate, furfural.
70. SULFURIC ACID and chlorates, perchlorates, permanganates.
71. VINYL ESTERS and alkalies (very exothermic).

STORAGE OF CHEMICALS

Containers of stored materials should be clearly labeled to show the identity of the contents.

The quantities of chemicals stored in a laboratory should always be kept to a minimum consistent with needs of the work. Arrangements should be made for isolated storage of chemicals in more than normal laboratory quantities. As soon as a job has been completed, the chemicals that were prepared as part of the job or obtained especially for the job should be discarded or placed in excess-chemical storage, except for reference samples that must be retained. Retained samples should be checked at regular intervals and discarded when no longer needed.

The properties of a chemical, frequency of use and quantity involved should all be carefully considered as bases for deciding where and how to store it. Stability, toxicity, and flammability are particularly important properties.

Refrigerated Storage

It is the responsibility of each chemist to determine whether a chemical is stable enough to be stored safely at room temperature or should be refrigerated.

SAFETY PRECAUTIONS FOR PILOT PLANT EXPLOSIVES LOADING OPERATIONS

GENERAL SAFETY REGULATIONS

The following general safety regulations apply to operations undertaken and involved in developmental loadings of high explosives. The safety instructions incorporated in this report are not meant to be all encompassing. Constant change in technology, applications to new materials and equipment, etc., necessitate that all proposed operations be examined very carefully as to potential hazards and as complete a safety instruction prepared as possible. The hazards of handling, mixing, etc., are usually easily defined and controlled. The hazards which are basically due to the chemical and physical nature of the explosive are usually more difficult to analyze. Prior to beginning any work impact sensitivity data, vacuum stability information and other sensitivity test data should be obtained. This information should be well known and understood by supervisors before starting work. Do not depend on data from laboratory scaled work, until such data has been substantiated by tests of plant produced material.

Hazards Should Be Understood

Possible hazards of every operation should be analyzed. Employees must know the nature of all work being done and the exact properties of all materials handled. Supervisors should inform employees of expected hazards and how to avoid them.

Hazards Should Be Kept To A Minimum

Keep to a minimum the amount of explosives handled; the number of persons and equipment exposed; and the exposure time. Posted limits of persons and equipment must be observed. Keep only minimum limited quantities of explosives and completed or partially loaded parts present at each stage of an operation.

Cleanliness

Personal cleanliness is important. Gloves and protective clothing are available and must be worn as operations require. Hands and face should be washed before all intermissions for smoking and for meals. Showers must be taken at the end of the working day as required when toxic explosives or materials are involved in operations.

Constant Individual Care

Habits of working must be formed correctly. New and unexpected hazards may develop; always be alert and on the look out for the conditions. Never assume that proper safety precautions have been taken. Make sure they have.

Housekeeping

All loading operations will be conducted in a neat and orderly manner with regular clean-up operations each day and a complete cleaning operation each weekend. Supervisors will insure good housekeeping and maintain effective policing throughout the loading area and surroundings. Effective cleaning methods will be used to minimize the accumulation of explosives or explosive dust and insure its removal from floors, walls, ceilings, ledges, tables, etc. A complete washdown of plant and equipment is advisable at set intervals throughout the year. The frequency of such washings will depend on the type of work carried out, degree of dust generated, etc. Periodic clean-ups must also include the "less obvious places" such as interiors of ducts and ventilators, overhead pipes, auxiliary equipment, bearings, etc. Pay particular attention to areas where explosives might be exposed to heat.

Receptacles For Storage Of Explosives And Explosive Parts

Keep explosives and explosive parts in approved covered receptacles, with covers in place when material is not being taken out of or put into the receptacles. Receptacles should be electrical conductors and when in use, be connected to a well grounded wire or placed on a well grounded metal plate. Inefficient and unnecessary transportation of explosives must be avoided.

Protection From Electro-Static Charges

Protect operations from electro-static charges by effectively grounding all machinery, equipment and fixtures, and, where necessary, employ suitable grounded conductive coverings for floors, work benches and tables and workers' conductive shoes. Workers' clothing of a type to minimize the accumulation of static-charges should be worn. This is of particular importance when handling materials developing dust, extremely sensitive explosives and inflammable solvents and should then be regarded as more than a routine regulation. Conductivity checks should be made periodically to insure that grounding wires, lightning protection, conductive floors, floor waxes, etc. provide sufficient grounding.

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Safety Equipment

Enforce the wearing of safety equipment, suitable safety footwear, goggles, gloves, respirators, hard hats and impregnated garments to protect personnel against burns, poisoning and associated industrial hazards.

Removal, Storage And Handling of Explosive

Explosive scrap produced during loading and later cleaning is usually removed from explosives loading plants by flushing with water to a draining system. Before the water stream leaves the loading area it must pass through a catch basin wherein the explosives are retained. Catch basins must be emptied periodically to prevent accumulation of dangerous amounts of explosives. These accumulations of explosives must not be allowed to dry and must be destroyed without delay. Heat evolving, and therefore dangerous, decomposition can be detected by temperature measurements.

Be extremely careful of reactivity between components in the catch basin. When hazards could possibly develop isolate catch basin scrap by cleaning immediately before and after special operations. Use extreme care in emptying scrap basins. Possible hazards are lack of oxygen and toxic gases in pits. Use sparkproof shovels, when friction sensitivity permits, otherwise wood or plastic tools.

Handling and storage of explosive scrap can be extremely dangerous. These basic rules should always be followed:

- (a) Unless it is known that explosives are compatible, do not allow one scrap explosive to be combined with another.
- (b) Scrap from sensitive explosives or scrap from explosives of unknown sensitivity should be kept to a minimum and disposed of frequently.
- (c) The amount of explosive scrap present must be included in the permitted amount of explosives. Therefore, in order to avoid inconvenient restriction of the amount of explosive working material, scrap should be removed frequently. Also, this should be done to keep amount of present explosives as much below the permitted limit as possible.
- (d) Do not use the plant scrap disposal system as a central gathering point for explosive scrap from allied facilities such as the chemical laboratory, etc.
- (e) Some explosives can be rendered less sensitive or more stable by removal of water soluble components. This should be considered when handling or storing explosive scrap.

NOLTR 61-138

There are no simple rules for magazine storage of many of the explosives involved in this work. Storage of materials not included in instructions in OP 5 should be guided by:

- (a) Keep the storage of potentially unstable material or material of questionable stability at a minimum.
- (b) Regard all new compositions with any potentialities at all toward instability as questionable and maintain a direct temperature record on the material as well as the magazine until experience has verified that it is stable. Keep in mind that a slight change in components, a change in an ingredient purity may place the explosive system from a stable to an unstable condition.
- (c) Be extremely suspicious of systems which do not have the vacuum stability characteristics of present explosives such as Composition B, and HBX.
- (d) Never store high energy materials of unknown stability with other explosives.
- (e) Do not store powdered metals with explosives or with other oxidizers.
- (f) Do not store oxidizers, i.e. ammonium perchlorate, ammonium nitrate, with explosives.
- (g) Explosives and high energy materials of low stability or unknown stability must be kept in isolation magazines and under close surveillance. It would be well to make arrangements to measure their temperatures remotely.
- (h) Be alert during all operations for any unusual gas, fumes, or odors such as the brown fumes of the nitric oxides, the odor of formaldehyde or chlorine. These indicate a reaction which could go out of control. Failure of the cooling system to keep the temperature below established maximum is a critical warning that the situation is getting out of control. This warning must never be ignored. Do something! Get out! Action in case any of these danger signals appear must be planned in advance. If no plans have been made in prior consultations with your supervisor leave the place with out delay.
- (i) When using solvents keep in mind that the toxic, flammable, or explosive characteristic may present a greater hazard than the explosive.

PREPARATION OF PROCEDURES AND INSTRUCTIONS

- (1) Job procedures for this type of work shall be written to include all available information on the chemical and engineering characteristics of the materials involved.
- (2) When procedures are released to a supervisor there shall be no deviation from the procedure except by authorization in writing by higher authority.
- (3) Operating instructions should be prepared for each unit of process equipment.
- (4) Operating instructions should be prepared for each task assigned. Where tasks are involved and consist of many non-related operations, the procedures should be tied to individual operations rather than the task. Whenever possible write a universal type of instruction applicable to a particular operation or task to avoid unnecessary instruction preparation. However, every task assigned must have an operating instruction, which may refer to the universal instruction.
- (5) A safety instruction must be included in the operating instruction for each task or operation. This portion of the operating instruction should be made conspicuous by underlining, printing with bold face type, separation in space, or other suitable means.

SAFETY PRECAUTIONS FOR UNIT OPERATIONS AND PROCESSES

Size Reduction

When small amounts of conventional explosive fines are required, for example in preparation of a sample for analysis, these may be produced by hand grinding using a mortar and pestle constructed of lignum vitae.

Oxidizer materials should be processed behind sufficient barricading to protect operators. Prior to milling make sure:

- (1) Material is free of contaminants and foreign materials.
- (2) Equipment is installed and maintained so that no lubricants can leak into the milling chamber or contaminate the oxidizer in any manner.

Mechanical size reduction should not be attempted on sensitive explosives systems such as perchlorate systems, explosive systems containing nitroglycerine, or on sensitive explosives such as RDX, HMX, PETN. Any reduction made by methods such as recrystallization should be

done prior to formulation. Explosive ingredients which are insensitive enough to permit reasonable safe milling should be milled before formulation of the explosive composition. Water or other inert dispersant should be used to decrease sensitivity during milling whenever possible or advisable. The sensitivity of the wet mixture should be determined prior to milling as the sensitivity is not always reduced by liquids.

Dispersion of explosive dust from dry milling must be prevented by dust collectors. Organic chemical dusts must not be dispersed in air because extremely violent explosions result if the dust in air is accidentally ignited. Provision must also be made for fire hazards.

Filtration

- (1) Provide the required protective clothing, respirators, etc., to prevent injuries from burns, toxic and inflammable solvents, etc.
- (2) When flammable solvents are involved, limit operator's quantities of solvent and explosive. Provide automatic sprinkler system fire protection. Use water soluble solvents such as acetone or alcohol if possible. The use of flammable solvents should be avoided if at all possible. The alternatives are water or toxic halogenated, usually chlorine containing compounds.
- (3) When filtering explosives use gravity flow. Do not use gear or piston pumps having metal working parts. If pumping is necessary use diaphragm or similar pumps with rubber or plastic parts. The effects of solvents, plastic parts, etc. on development of static charges should be considered. The compatibility of the explosives with solvents and equipment parts with which they make contact must be considered.

Blending

- (1) Avoid the generation of explosive dust by the use of ventilation, dust collector systems, etc.
- (2) Consider sensitivity levels prior to deciding on the procedure and safety precautions and utilize remote control operations where necessary.

Size Separation

Do not attempt to dry screen explosives in the sensitivity range of HDX, PETN. When size separation is necessary, use a wet screening method, settling method or other safe process.

Crystallization

- (1) Select water soluble solvents when possible.
- (2) Provide sprinkler system protection when flammable solvents are involved.
- (3) Control toxic hazard levels of solvents by proper selection of solvents.

Drying

- (1) Determine whether a remote control operation is necessary.
- (2) Determine that drying will not increase sensitivity.
- (3) Determine that drying will not create a reactive material with possible decomposition.
- (4) Take steps to eliminate solvent vapors from the area.

General Summary

- (1) Avoid handling of dry, sensitive explosives or explosive formulations. Do not begin blending, mixing or grinding operations on explosives without first establishing an effective pre-inspection operation.
- (2) Equipment installation should be based on strict compliance with all electrical codes.
- (3) Insure that explosives are compatible with solvents.
- (4) Use toxic or inflammable solvents only when necessary.
- (5) Avoid use of non-conductive containers for inflammable solvents and explosive sensitive to static-charges.
- (6) Keep oxidizers from organic materials, except in process. If possible add the oxidizer to the formulation last. In some cases maximum sensitivity is developed by the addition of the explosive; in that case, add it last.

SAFETY PRECAUTIONS INVOLVED IN PREPARATION FOR LOADING

Ordnance, Explosive Charge Containers, Etc.

- (1) The explosive load must be protected:
 - (a) From metals, plastics, etc., coatings with which it may react

- (b) From the danger of pinching, friction, etc.
 - (c) From detonation or deflagration in case the container ruptures or is damaged when dropped, struck, etc.
- (2) Ordnance should be examined and when required the explosive cavity should be lined with a suitable, compatible lining material such as compound, asphaltic, hot melt, MIL-C-3301 or coating compound, bituminous, MIL-C-4504, or some other suitable lining approved, applied to the required thickness and uniformity. Explosive charge container assemblies should be designed to provide a safe unit under the expected loading, handling and storage conditions.

Molds, Pressing Die, Etc.

- (1) Prior to use all molds and dies should be examined to insure that no development of friction or pinching action against the explosive will occur.
- (2) Materials of construction and surface finish should be selected so as to insure easy disassembly and easy removal of the charge from the mold.
- (3) Materials of construction and explosive being pressed or cast should be selected to eliminate the use of any materials which will or could possibly react with the explosive, produce a sensitive charge, etc.
- (4) Materials of construction and design must insure that there will be no distortion under applicable loads.

SAFETY PRECAUTIONS FOR INSPECTION AND WEIGHING

All explosive materials and ingredients included in explosive compositions should be given an effective inspection for contaminating substances. Inspection may be visual (if effective) or by screening. All materials should be passed over permanent magnets of sufficient strength to remove all contamination of a ferrous metal nature unless previous inspection at the packaging facility makes this unnecessary. Screen when used as inspection equipment should be of a mesh only slightly larger than the size of the material being inspected.

All ingredients must be compatible with the explosive in the explosive system.

Containers should be conductive when used for storage of materials sensitive to static discharge or which easily create a dust sensitive to static discharge. In general, containers should be fabricated of strong fiber or plastic material compatible with explosives or of soft aluminum. Containers should be fitted with a hinged lid to permit easy closure and should be of a seamless construction.

Unless impractical, explosives in the sensitivity range of HDX should be used water wet. When this is impossible because of problems in obtaining exact weights, etc., dry RDX, HMX, PETN and similar hazardous explosives should be handled and stored in seamless rubber or plastic containers, preferably conductive. Operations should be arranged so that the material, once prepared, is subject to a minimum of carefully supervised transfers. If extended storage is necessary, restow under water as instructed in OP 5. Take whatever steps are necessary to insure that containers of HDX, etc. are not dropped.

SAFETY PRECAUTIONS FOR MIXING AND BATCHING OPERATIONS

These operations are divided into two areas of hazard: those which may be accomplished without barricade protection and those which should be completed only under remote control conditions.

Barricade Protection Not Required

(a) Prior to initiation of work:

1. Insure that equipment is in good working condition and clean.
2. Make sure that agitator clearance is correct at maximum operating temperature.
3. Make sure that temperature sensing and recording instruments are operating correctly.
4. Heating fluid should be limited in temperature by a suitable automatic control device to stay well below the temperature level at which thermal decomposition of the systems begins.

(b) Charging Ingredients

1. Preheat unit. Note: Where possible, swirl breakers should be installed so as to be heated with steam or hot water.
2. Always add the materials which provide the liquid phase first.
3. Control rate of heating and addition of ingredients so as to avoid chance of producing large lumps of explosive.
4. Use extreme caution in addition of materials which, due to high heat capacity or rapid heat conduction, could cause the batch to solidify.
5. Avoid creation of dust by good ventilation.

6. RDX and explosives of similar sensitivity should be handled water wet whenever possible. The water can be driven off later by extended heating to the batch, by vacuum drying, etc.

(c) Vacuum Treatment

1. Insure that drop valves, etc. are constructed to prevent leakage of explosive onto working parts.

2. Keep vacuum lines clean. Inspect as often as necessary to insure that they are clean. Install traps if necessary.

3. Insure that there is an effective filter between kettle and pump. Clean as often as necessary to maintain filter medium effective.

4. Set-up a routine on oil change for pump and adhere to change periods. Check oil visually daily to insure that filter is operating.

5. For the conventional explosive systems: Composition B, HEX explosives, TNT, tritonol, picratol, cyclotols and octols there is no need for a liquids trap, however, this must be considered for other systems and installed where vapor pressure, temperature, reaction products, etc., show a need for it.

Mixing Operations Requiring Remote Control

(a) Determine whether or not a composition belongs in this category by examination of sensitivity data both of the mixture and individual explosive ingredients, any available accident data on it or similar systems, type of mixing operation, possible reactivity, etc.

(b) These and similar systems should always be remotely mixed or compounded until experience shows the process to be safe:

1. Formulations containing appreciable nitrocellulose.

2. Formulations containing nitroglycerine.

3. Any mixture of an oxidizer, i.e. ammonium perchlorate, ammonium nitrate, etc., and an organic explosive with or without a metal should be looked upon with suspicion. An oxidizer with an organic chemical may also be explosive.

4. Any mixture with a sensitivity in the range of RDX.

5. Any mixture of an oxidizer and metal.

(c) The folliuring and similar equipment should also be operated by remote control when mixing explosives.

1. Fan mixers
2. Mixing rolls
3. Kneaders, Sigma mixers, etc. (vertical or horizontal type)

(d) All new explosive compositions or new explosives should be examined as a pilot plant mix not a laboratory mix for sensitivity before being adjudged safe for processing except under remote control conditions.

(e) Since the materials used will be extremely sensitive it is very important to make sure that mixer rotor blades have sufficient clearance, that close fitting or rubbing parts are eliminated and that bearings or glands are always outboard of the mixer where contamination with explosives can not occur. Clearance should be sufficient to allow for loading and temperature changes.

SAFETY PRECAUTIONS FOR LOADING

Loading Operations Environment

- (a) Maintain high standards of housekeeping throughout all operations.
- (b) Thoroughly clean equipment after each operation.
- (c) Use flexible conductive rubber buckets when containers are necessary in transferring explosives and rubber is a satisfactory material.
- (d) Avoid spillage.
- (e) Use wood or soft aluminum rods when required in the loading operation, reactivity of the explosive permitting.
- (f) Have available full protection to employees - gloves, protective clothing (flame proof), face shields, safety glasses, face masks, respirators, etc., and insure that protective gear be used as required.
- (g) Limit personnel to those necessary to job and keep amount of explosives to a minimum.

Keep chamber clean.

b. See page 55, "Vacuum Techniques"

using

(a) All explosive pressure operations should be done under remote control conditions.

(b) Check out die assembly working pressure and lubricate with 2% graphite before using die for loading.

~~Perform all operations involved including loading under remote control conditions.~~

~~(c) Explosives wait at least one minute prior to leaving assembly area until removal of die parts or removal of the charge.~~

~~(d) When ejection of explosive material occurs, wear ear plugs, etc., when conditions are such that these protective devices cannot prevent injury in case of accidental detonation.~~

~~LOADING~~
SAFETY PRECAUTIONS FOR OPERATIONS A

(1) Insure that fasteners, etc., are not contaminated with explosives before disassembling molds, etc.

(2) Perform all machining, sawing, shaping operations on explosives under remote control conditions until experience, evaluation of problems and sensitivity data show operation need not be remotely controlled.

(3) Disassembly of explosive loaded ordnance should be considered a remote control operation if there is any question of hazard in the operation.

(4) Be extremely careful in the removal of risers and riser frames, etc. that explosive is not crimped between metal surfaces.

SAFETY PRECAUTIONS FOR ASSEMBLY

(1) All assembly operations involving crimping operations on explosives such as booster cups, etc., should be done under remote control conditions.

(2) Although routine in nature, assembly of cover plates, fuze wells, etc. is extremely dangerous work unless supervisors insist and control the decontamination of all threaded fittings and openings and places where explosive can be subject to extreme forces and friction.

(3) The liberal use of a compatible grease is a valuable adjunct to safety in assemblies when there is a chance of contamination.

GENERAL SAFETY PRECAUTIONS FOR MATERIALS

(1) When powdered metals are used as a component of an explosive, surface treatment of the metal may be required to reduce reactivity. For instance the dichromating process will form a non-reactive coating on atomized aluminum.

(2) It should be realized that materials which are normally desensitizers to explosives can become sensitizing agents when used in other explosive systems. For instance wax used as a desensitizer for HBX explosives will function as a sensitizer or as an explosive component when used with ammonium perchlorate. Do not apply information valid for one explosive system to another without careful study and testing.

(3) As part of explosive assembly operations, use is being made of the latest adhesives, cements and fillers, including the epoxies and polyesters. These materials can be very toxic, dangerously reactive and fire hazards, see references (21) through (25).

PYROTECHNICS

INTRODUCTION

Pyrotechnic compositions are physical mixtures of finely powdered chemical compounds and elements which, when ignited, can readily undergo combustion (chemical reaction) with the evolution of a considerable amount of heat and light in a relatively short period of time. Various organic binders and color intensifiers may be included in the mixtures. The reaction may be accompanied by smoke and/or sound. The heat of reaction for one gram of pyrotechnic composition may range from 200 to 2,500 calories per gram which represents an appreciable amount of energy. This amount of energy, while considerable and often extremely dangerous, is not generally released in so destructive a fashion as the energy of explosives, except in the case of photoflash compositions and loose illuminant and igniter compositions. This is so because of the relatively low burning rates usually required of pressed pyrotechnic compositions and the fact that only a relatively small proportion of the reaction products are gaseous, so that the released energy is dissipated as heat and not converted to mechanical energy. However, in the research and development of pyrotechnic compositions, it must be remembered that loose compositions such as photoflash mixtures, igniter, and fast burning illuminant compositions may react with destructive violence.

This is due essentially to these factors (1) the amount of air contained in the sample as well as the gaseous products of the reaction, (2) the great speed at which the energy may sometimes be released and (3) the high heat of reaction; all these factors favor shock wave formation and, thus, destructive effect. The temperatures reached during the reactions which take place in pyrotechnic compositions range from 1000°C to over 3500°C.

SAFETY PRECAUTIONS FOR WORK WITH PYROTECHNICS

Hazards Must Be Understood

Before undertaking a project all details must be analyzed and thoroughly understood. The chemist or chemical engineer should write a plan of operations with particular attention to pertinent safety precautions to avoid all hazards. The plan must be discussed with the supervisor. If available equipment or facilities are deemed inadequate for safe operation as planned, the supervisor should be so informed at this time. Defects of facilities and equipment will be corrected before proceeding with operations in accordance with the plan.

Safety Equipment Used in the Pyrotechnic Laboratory

- (a) Static proof by grounding all equipment such as tables, scales, ovens, processing and pressing equipment. Cover floors with a conductive, non-sparking material.
- (b) All electrical apparatus and wiring shall be as specified by Article 4409 of reference (22).
- (c) Non-ferrous spark proof tools shall be used in the laboratory.
- (d) Ovens shall be equipped with covered heating coils and explosion proof latches. The ovens shall be equipped with double thermostat controls to prevent overheating due to a faulty control. The relays, actuated by the thermostats, should be set for "normally open" operation with respect to heating power supply.
- (e) Hoods in the laboratory shall be equipped with a 1/2" thick laminated safety glass.
- (f) Operators shall wear fire resistant coats and other fire resistant apparel as necessary. Silk, wool, rayon or other types of clothing known to readily produce static electric charges shall not be worn. All operators in a pyrotechnic laboratory shall wear approved conductive soled, non-sparking safety shoes at all times. Approved safety glasses or goggles shall be worn at all times. Grounded bracelets shall be worn when working.

with static electric sensitive materials. When the work involves experimental compositions which may flash or explode, the operator shall be equipped with fire resistant gloves and an approved safety shield. The safety shield should be interposed between the operator's face and the source of hazard. A face shield worn so that a flash could come up under the shield may be worse than wearing no shield.

(g) Fire-fighting equipment - All laboratories shall be equipped with approved fire extinguishers placed in strategic locations. The employees should be trained in the use of the extinguishers and each employee should be assigned a station. Fire blankets and safety showers should be strategically located in the laboratory. No attempt should be made to extinguish any fire that causes any danger of an explosion. Everyone should evacuate the laboratory or work area in accord with a plan established after practice fire drills.

Safe Operational Procedures in Pyrotechnic Laboratory

(a) Limit the degree of hazard involved by conducting initial experiments with the smallest amount of material possible. Properties of new formulations which should be determined are: compatibility of ingredients, electrostatic sensitivity, impact sensitivity, friction sensitivity, ignition temperature, and vacuum stability at a suitable temperature. Keep the results of these sensitivity tests on record along with any other information pertinent to the safe handling of the compositions. See that this information is passed on for use in prototype and production operations.

(b) Quantity limits for rooms and areas should be established and those limits should never be exceeded. This rule is not to be construed to excuse the presence of quantities larger than necessary for the work at hand, even though the limits are not exceeded.

(c) Pyrotechnics, like explosives, under the right conditions can release tremendous amounts of energy per small unit of weight. Experiments should never be left unattended and if the material is likely to be hazardous a placard should be mounted notifying fellow workers of the type of material and the hazards involved.

(d) Pyrotechnic compositions must not be ground or crushed by any method which may cause impact or friction. If the material is very sensitive, the wet method of mixing should be used. Quantity mixing must always be controlled remotely. Small scale mixing should also be remotely controlled. Mixers should be provided with means for remotely controlled discharge of mixer contents. If observation of these or any other operations remotely controlled is required or desired, the Naval Ordnance Laboratory, White Oak, Md., highly recommends closed circuit television. Non-flammable

solvents should be used in this method of mixing. High order explosions have been caused by the use of flammable solvents such as acetone.

(e) Never charge ovens with incompatible materials. Avoid leaving sensitive materials in laboratory ovens over-night and over the weekend.

(f) Extremely sensitive materials should be dried in a high vacuum at temperature not to exceed 60°C.

(g) No experimental or hazardous laboratory work shall be conducted in the pyrotechnic laboratory unless two people are present and at least one of these must be experienced in work with pyrotechnics. These two must be separated so that the danger of both being injured by the same accident is avoided as much as possible.

(h) Good housekeeping shall be observed at all times. Materials spilled shall be cleaned up immediately. The individual working areas shall be cleaned up at the close of every working day. Residual chemicals or compositions shall never be thrown in waste baskets, general purpose waste disposal cans or down drains. Waste materials shall be kept segregated and sent to the burning pit at frequent intervals along with a scrap report itemizing the materials being scrapped.

(i) Avoid physiological hazards. Many of the pyrotechnic components can produce harmful physiological effects if the materials are inhaled as a dust, ingested by way of the mouth, or if allowed to come in contact with the skin. Wear approved respirators in dusty operations. Eating shall not be allowed in the laboratory proper. Approved protective clothing shall be worn to reduce skin contact with pyrotechnic materials. Wherever possible dusty operations shall be performed in a hood equipped with a good exhaust system. Laboratory workers shall wash thoroughly before lunch and at the end of the working day to remove any traces of materials which may cause adverse physiological effects.

Hazards in the Specific Pyrotechnic Fields

The pyrotechnic compositions are used as illuminants, smokes, flares, delays, igniters, infrared flares, incendiaries, tracers, heat powders, photoflash, and simulated ammunition compositions.

Illuminating Compositions

These compositions consist of a finely divided metal, an oxidizer and a binder. These compositions are sensitive to impact, friction, static electricity, open flames or sparks. The usual metals employed are magnesium and aluminum or any alloy of the two. Sodium nitrate is commonly used as the oxidizer. Paraffin used as a binder in older formulations has been

largely supplanted by synthetic resins. Even the standard illuminating compositions can be very hazardous. Their potential energy under the right circumstances can be released with destructive violence. Experimental compositions can be even more hazardous. Initial experiments should involve the smallest amounts possible until sensitivity tests are run to determine the extent of the potential hazard. Operations involving these compositions should be conducted behind 1/2" thick laminated safety glass, equivalent, or better.

Mixing

Illuminating compositions shall not be mixed by means of the mortar and pestle or by any other means which would subject the material to friction or impact. All apparatus used in mixing the compositions should be well grounded. Spark proof materials should be employed whenever possible.

The oxidant and the metal should not be mixed dry unless a non-friction type of mixing can be employed. (Ten pounds of sodium nitrate and magnesium detonated, destroying a 36" Simpson mixer and creating extensive damage to 18" thick concrete walls). The safer procedure is to coat the metal with the binder prior to adding the oxidizer.

The newer binders used in illuminating compounds usually consist of a synthetic resin, a polymerization agent, and a catalyst. The chemist or technician shall be thoroughly acquainted with the chemical, toxicological, and explosive hazards involved in work with these binders. The proper time for addition of accelerator must be determined.

Flammable solvents shall not be added to illuminating compositions to improve mixing procedures. Such a mixture with acetone added to the binder has been known to produce an explosion of high order.

Pressing

All molds and tools shall be of spark proof-materials. Molds and rams are inspected before use to insure they contain no foreign material and that they are free from burrs which might cause friction. The mold shall be placed in the holding device and the ram brought down to check for proper alignment. The pressing shall be performed behind a 1/2" thick laminated safety glass and when possible by remote control. If the body being pressed contains more than one composition, keep the compositions separated, preferably by baffles. The weighing of the compositions shall be performed at a safety distance from the pressing operations. Pressed bodies shall not be allowed to accumulate but shall be removed from the immediate pressing area as they are completed. The base of the press and the working area shall be swept at frequent intervals with static proof brushes to remove any blow-by or spilled compositions. Ram removal must be remotely controlled.

Smoke Producing Compositions

These pyrotechnic signal compositions are designed to burn to produce as much smoke as possible. Burning usually takes place less energetically than with other types of pyrotechnics because at lower temperatures less of the solid smoke particles are consumed. Nevertheless, the precautions applied to mixing and pressing illuminants and flares must also be observed in mixing and pressing smoke compositions.

There are several hazards that should be the subjects of warnings to those who work with smoke compositions. First, some of the smoke compositions contain red phosphorus. Precautions which must be observed in working with red phosphorus in order to avoid fire or injury are described in detail in a later section of this manual.

Another special group of hazards is introduced by the use of salts or chloric acid, the chlorates. Potassium chlorate is the chlorate generally used. The chlorates almost always increase sensitivities of smoke compositions to impact or blows. Also compositions containing chlorates usually can be very easily ignited. These effects were discussed by Irving Kabik in reference (26).

Some of the ingredients of smoke compositions introduce special physiological hazards, especially the dyes used in colored smokes. Specific information about the toxic properties of these dyes and of other ingredients can usually be obtained from their makers, reference (27).

Other instructions about production and testing smoke compositions are given below.

As noted potassium chlorate can form dangerous explosive mixtures with organic compounds. For this reason smokes should be mixed in two stages: Make a premix of retardant and oxidizers, to this premix add the fuel, dyes and volatile solvent. After mixing and prior to granulation, the smoke compositions should be dried to complete evaporation of the volatile solvents. If the composition is dried in an oven, a forced draft oven heated by steam coils or a vacuum oven should be used at temperatures below 60°C.

Inasmuch as smoke compositions may present explosive hazards their impact sensitivity must be determined before production is undertaken or begun.

Before experimenting with red phosphorus formulas read the hazards and precautionary measures listed under red phosphorus. The main hazard to be avoided is the ignition of the phosphorus or its compositions by spark or friction. Do not use brushes with metal ferrules around the precision balances while weighing red phosphorus.

Flare Compositions

Flare compositions are designed to produce white and colored light in various signaling devices. A typical flare formula is that used to produce the red flare. It consists of potassium perchlorate, strontium nitrate, magnesium coated with paraffin, hexachlorobenzene and gilsonite. The flare formulas are similar in sensitivity to the illuminants. All the precautions observed under illuminating compositions should be strictly adhered to. Chlorate and perchlorate oxidizers are commonly used because they are also color intensifiers. The hazardous properties of these two classes of compounds are given in reference (26)

All of the safety precautions listed under the chlorates and perchlorates must be strictly adhered to. The fuels and binders are premixed, the oxidizers and other components are premixed, and the two premixes blended to form the flare compositions.

Delay Compositions

Delay compositions commonly used are the so called gasless type, consisting of a metal as a fuel and chromates as the oxidizer. The sensitivity of delay compositions is similar to that of the flares and illuminants. Experimental delay powders can be very hazardous depending on the metal used, its micron size, and the oxidizers used. Delay work is made more hazardous because many of the delay compositions require very sensitive igniters.

Mixing operations should be performed using remotely controlled, non-friction type of mixers installed behind adequate shielding.

Operators should be equipped with proper clothing and safety devices including fire proof gloves, conductive soled safety shoes, safety glasses or face shield and grounded bracelets.

Experimental formulations mixed by hand should not exceed 5 grams until sensitivity tests are run to determine the hazards involved. These experimental formulations if they must be mixed by hand should be performed in the hood behind laminated safety glass with the exhaust system on. No mixing operations should be performed by a grinding or crushing action.

During weighing of delays keep the components separated sufficiently far apart and separated by baffles to avoid a spark jumping from one container to another. Test grounding devices. Use spark proof spatulas. Keep a safe distance between weighing and pressing operations. Limit components to 25 grams.

During pressing, observe the same safety precautions recommended for pressing illuminants. Remove pressed delays from pressing area.

Use static proof brushes frequently to remove any spilled composition around weighing or pressing areas. Operate press from behind 1/2" thick laminated safety glass.

Igniters

The same precautions should be observed in igniter work as for illuminants and flares. When titanium, zirconium or other similar fuels are used greater precautions must be taken. These ignition compositions using titanium and zirconium, or other very sensitive fuels, should be mixed under a non-flammable solvent, if possible. The ignition devices should be loaded wet and the units dried in a vacuum oven under argon.

Zirconium and titanium compositions are very sensitive to static electricity and may be exploded by a static electric spark. Zirconium and lead dioxide igniter compositions are examples of very sensitive compositions and have been known to explode. Boron and potassium nitrate have been known to explode causing injury to workers, as can any finely divided fuel and an oxidizer.

Infrared flares are compositions consisting of a finely divided metal and oxidizers selected to emit energy in the infrared region. Safety precautions observed in illuminant and flare operations are applicable. Remotely controlled mixing is mandatory. Extra caution must be observed in avoiding breathing of the fumes from the burning flares since they are very toxic.

Tracer compositions consist of an oxidant, a fuel and a binder. A typical composition consists of a finely powdered metallic fuel, strontium nitrate oxidant, and polyvinyl chloride binder and color intensifier. The same precautions observed for illuminating compositions shall be observed for tracer mixes.

Photoflash compositions are composed of finely divided metals, an oxidant, and a depressant. A typical composition consists of powdered aluminum, barium nitrate, and calcium stearate. Such mixtures are very sensitive and can detonate with great violence. All of the explosive and pyrotechnic safety rules should be observed in photoflash operations.

Heat powders consist of high energy metallic fuels and oxidizers, usually chromates. A study of reference (26) will indicate the hazards involved in handling the components. All the pyrotechnic safety regulations must be followed, with particular attention to protecting operations against static electricity or sparks of any kind.

Incendiaries may involve pyrophoric fuels, phosphorus compositions, thermite mixtures, jelled gasoline, or other organic fuels. Fire hazards are of the highest order; explosive and physiological hazards are also involved. All explosive and pyrotechnic safety regulations must be followed.

Chemicals

A large and important part of the knowledge required to insure the safety of those working with high energy materials is a complete knowledge of the properties of the specific chemicals used. Because the list of chemical materials for the production of explosives, propellants, and pyrotechnics is long, and growing longer, it is not possible to include a satisfactory list. Also, it is not believed possible to include a complete list of chemicals for pyrotechnics together with the information required about these materials. Much more comprehensive information can be obtained from a text such as reference (2). The bibliography herein gives many sources of information about the dangerous properties of chemicals and how workers may be protected. Many of these sources are chemical manufacturers from whom current information about their products can be obtained.

Red Phosphorus

Red phosphorus is an important and frequently used ingredient of pyrotechnic compositions. Because it introduces a variety of technical hazards some of these are described below together with ways of guarding workers against the hazards.

It is a dangerous fire hazard. It causes many of the toxic symptoms of "white" phosphorus, commercially called yellow phosphorus. It is easily ignited by spark or friction. If the white phosphorus content is excessive it may ignite spontaneously when exposed to air. It is dangerous if ingested in quantity, or if small amounts are allowed to get into the body over a long period of time. It should never be allowed to come into contact with the eyes.

Precautions

Keep adequate supplies of sand and water on hand to extinguish fires. In case of a red phosphorus fire, saturate it with water or sand immediately. Do not attempt additional operations in any area where a fire has occurred until thorough decontamination has been completed.

In case of a fire involving people, extinguish the fire with copious supplies of water. If burning phosphorus has come into contact with clothing, either remove it or keep it wet.

For decontamination of work areas following a red phosphorus fire:
(1) The bulk of the partially burned or contaminated material should be moved to a proper place for safe burning, all the while keeping the partially burned material saturated with water during movement. (2) Wash down area with large amounts of water, then wipe down walls and floors with a vegetable oil. (3) Inspect the building after dark for white phosphorus residues when their phosphorescence makes them visible.

Keep any area of the body which has been in contact with burning phosphorus wet or submerged in water. Wash the burned area in 5% solution of copper sulfate and obtain a physician's services immediately. Do not apply unauthorized salves, ointments, or greases as they only spread the contamination.

If red phosphorus enters the eye, wash it out using a bubble type fountain or inverted faucet. Use large quantities of water. Then irrigate the eye with castor oil. Do not use copper sulfate solution in the eyes.

If burning red phosphorus enters the eye, wash eye out with water and call a doctor right away. Continue washing eye till doctor arrives.

Small bandages impregnated with copper sulfate should always be on hand when red phosphorus is present.

Keep work areas clean. Dump contaminated material immediately in water.

Use only non-ferrous tools to open red phosphorus containers to avoid hot sparks. Wear a pad respirator when handling bulk red phosphorus.

Keep hands away from face and wash thoroughly before eating. Do not eat, drink, chew gum or tobacco or anything else while in a red phosphorus area since ingestion of red phosphorus may cause severe toxic symptoms.

Never mix waste material from a red phosphorus operation with other waste materials, since this may result in fire or explosion.

Persons working with red phosphorus must not enter buildings other than those designated for red phosphorus work, since contaminated clothing and shoes could result in a serious fire. Clean equipment and work areas thoroughly at the end of each day for prevention of fire.

For decontamination of work equipment:

1. Remove material as stated above in step number one.
2. Disassemble equipment and clean all parts with trichloroethylene in a properly ventilated work area.
3. Allow parts to dry for 16 hours.

PROPELLANTS

INTRODUCTION

Solid propellants, like pyrotechnics, to be effective must release substantial quantities of energy as heat plus large volumes of gases. The energy of propellants is released during longer periods of time than the energy of explosives. In spite of this slower energy release from propellants it is fast enough so that in case of accident the resulting destruction may appear to be equal to that of an explosion. In fact, after viewing an accident involving propellants, it is often very difficult to believe that an explosion did not occur, and in fact, explosions do occur.

The hazards of propellant processing may be greater than the hazards associated with the finished product. Also there may be hazards associated with processing a new propellant composition that have never been previously encountered. Therefore, essential information for insurance of safety must be obtained by working on a small scale and by exhaustive tests of the product before undertaking larger scale work.

The Naval Propellant Plant designed the following procedures for obtaining such essential information at each and every stage of operations.

SAFETY PRECAUTIONS USED FOR PRELIMINARY MIXING AND TESTING
OF NEW PROPELLANT INGREDIENTS

General

In preparing a sample for tests, and testing, to evaluate a new propellant ingredient it is assumed that safety hazards exist in all stages such as grinding, mixing and heating.

Specific Test and Procedures for Propellants

- (a) Impact sensitivity tests are made on all samples before handling.
- (b) Friction sensitivity tests are made on all samples before handling.
- (c) When a sample indicates a high degree of sensitivity to impact or friction, express authorization should be obtained from the person in charge of the project before attempting to grind, mix, or heat the material, and if so authorized, maximum attention to safety precautions must be maintained.
- (d) Grinding is done in a ball mill operated by remote control and located behind a safety shield. No more than 5-10 gram quantity is ground at any one time.
- (e) Mixing is done for two hours in a container attached to and tumbled end-over-end by a 6 rpm motor, remotely controlled, and located in an exhaust hood and behind a safety shield. No more than a total of 1-2 grams of an ingredient or mixture of ingredients is processed at a time.
- (f) Ignition or explosion temperature is measured by heating a 1 g. sample in a test tube held in an aluminum block wherein a thermometer and an electrical heating unit are contained. The assembly is located in an exhaust hood behind a safety shield. The rate of temperature rise is controlled by a remotely located 5 ampere variac. A cathetometer remotely located is used to make the temperature readings.
- (g) The temperature at which the sample ignites or explodes and any other preliminary test data are tabulated to provide an evaluation of the hazards in handling and using a particular ingredient.

Safety Equipment

Goggles, gloves, aprons, masks, safety shoes, safety shields, remotely controlled apparatus, wire screening and exhaust hoods are to be worn or used unless experience indicates such are not needed.

PROCESS REVIEW

General

Prior to the development of any process beyond laboratory stage that is a departure from an established program, a Process Review Board should consider it carefully. This board should review all known characteristics and properties of the ingredients and steps to assure their control.

Pilot Plant work will not proceed until this board has given its approval. In turn such processes will not proceed from pilot plant stage into scaled-up production until this board has reconvened and evaluated findings from pilot plant work.

Functions and Responsibility of Review Board

The board will review critically all findings from tests, studies, and evaluations to determine adequacy and reliability of information supplied or required by this Section. Following appraisal, it will prepare a record report recommending approval of proposed action or modification to proposal for submission to Management for final action. The Review Board will determine adequacy of the following:

- (1) Knowledge of physical and chemical properties.
- (2) Hazardous information relating to materials produced and the process controls from a toxic, fire and explosion standpoint.
- (3) Analytical procedures and control techniques, etc.
- (4) Surveillance procedures during storage to detect possible breakdown or degradation.
- (5) Handling and transportation methods.
- (6) Waste disposal methods.

Board Membership

The board, as proposed by the Naval Propellant Plant, should be composed of the following with modification made to adapt it to organization of other establishments.

- (1) One analytical chemist.
- (2) One Safety Engineer or Safety Officer
- (3) Head of Inspection or Quality Evaluation Division
- (4) Director of Pilot Plant or Director of Production

Meetings

The board will convene on call of the chairman following proposal to proceed in development from laboratory to pilot plant or proposal to proceed from pilot plant into production.

FUNDAMENTALS OF SAFETY FOR EXPERIMENTAL
PROCESSING, HANDLING AND STORAGE OF
HIGH ENERGY MATERIALS

This section of this report was contributed by the Naval Ordnance Test Station. It expresses ideas of the fundamentals of actions which will insure safe operation in the laboratory, in the pilot plant, and in the plant where production of high energy material is being established.

PREFACE

Research and development organizations, such as the Naval Ordnance Test Station, doing work on new propellants, high explosives, pyrotechnics, and other high energy materials have attempted to abide by safety rules and safety guidelines developed primarily for production organizations. While this procedure has worked reasonably well in the past, there is concern about the adequacy of current safety guides for the present and the future. Guidelines developed for production tend to fit well known materials and well established practices but they cannot be expected to deal adequately with all problems in new areas of work. We have entered into a period of rapid changes where the materials being worked on are considerably different and some are more hazardous than the materials worked on in the past. Therefore, it is believed that changes are needed in the approach to safety in research and development organizations. It is also believed that research and development organizations need guidelines that are flexible and allow safety decisions to be made as close to the point of greatest information as possible. In the final analysis, it is necessary to depend on the personnel working with new materials to analyze their safety problems and develop safe procedures for new areas of work where there are no exact precedents.

INTRODUCTION

The objectives of a good safety program for work on high-energy materials are:

- (1) To minimize hazards to personnel and prevent loss of lives.
- (2) To prevent accidental fires or detonations.
- (3) To minimize possible loss of equipment and buildings.
- (4) To reduce accidents typically occurring in almost any laboratory or operation.

The following statements are general guidelines that are relevant to work on almost every material that is capable of sudden release of chemical energy and chemical products in sufficient amounts to be harmful or dangerous.

These guidelines are an organized set of fundamentals of safety on which there is general agreement, among experienced technical, safety, and supervisory people, that the fundamentals are an applicable and necessary part of an explosive safety program. These fundamentals avoid stating exactly how an organization is to perform its responsibilities, but they do attempt to point out what the responsibilities are and to offer general suggestions of the important factors to be considered in hazardous work with high-energy materials. The fundamentals by themselves are just a starting point; they must be put to work and given concrete meaning through thought, discussion, and training sessions. Safety in any situation calls for knowledge of the characteristics of the materials being worked on, knowledge of the behavior and characteristics of equipment and its possible interactions with high-energy materials, knowledge of the characteristics of people as they are, and knowledge of how to design and maintain facilities and equipment for safety.

These safety fundamentals are intended as guides for preparation of instructions and rules for specific applications and as guides for training personnel connected with work on high-energy materials. They were prepared for use by research and development groups working on high-energy materials in amounts ranging from a few grams to full scale pilot plant quantities.

The phrase "high-energy materials and the word explosives" are used here to cover the broad field of propellants, high explosives, pyrotechnics, and primary and initiating explosives.

General Fundamentals

Accidents with explosives are caused by energy concentrations, such as sparks, friction, impact, flame, hot objects, chemical reaction, radiation, excessive pressure, and electro-static discharge. Energy concentrations anywhere near initiating levels must be kept away from explosives except when it is desired to ignite or detonate the explosive.

The initiation of explosives is subject to probability considerations. With a low level of stimulus, the probability of initiation can be small; with a high energy concentration, the probability of initiation will be much larger but still not certain. The probabilities at the extremes cannot be determined with accuracy from a small number of tests. Therefore, in order to keep the probability of initiation low, it is good practice to treat explosives as gently and as carefully as possible.

The above concept of probability is applicable to accidents in general, because accidents often involve a series of events that must be fulfilled for the accident to occur. One purpose of a safety program is to keep the chain of events broken.

When specific knowledge is lacking on the characteristics of an explosive, the worst characteristics that might affect safety must be assumed.

Explosives that are new to an individual or group working with them must be regarded as extremely dangerous until their characteristics are well known and the individual or group has become skilled in practices that minimize processing and handling hazards.

Personnel Training and Protection

Important elements of safety are the formation of good habits; a calm, mature environment; and training based on previous experience in the whole explosive field.

All supervisors of explosive operations must have adequate training and knowledge to maintain safety of operations.

A man performing an explosive operation without direct supervision must have sufficient training and knowledge to maintain safety of his operation.

Persons working with explosives must be safety minded and emotionally stable.

For persons working with explosives or observing explosive operations, provide protection for their eyes, protection against fire or intense radiant heat, means for automatically discharging static electricity from their bodies, and means for keeping their bodies and personal clothing free of contamination.

Means must be provided for safeguarding personnel from toxic materials, fumes, or other harmful effects. With very toxic materials, there may be need for protecting people considerable distances away who may or may not be involved in the work.

Provide showers, eye washers, and other first-aid devices, which are necessary immediate aids in preventing further injury, in locations that are quickly and easily accessible.

Personnel working with toxic materials must be given periodic medical examinations.

Adequate tools and help for lifting, for performing operations, and for emergency assistance should be available.

Visitors unfamiliar with explosive operations or the explosive facility must be escorted by a responsible person who knows what is going on and what the safety precautions are.

Planning and Preparation

Data on properties and characteristics of new explosives to be processed in larger than minimum laboratory amounts should be reviewed by a qualified group prior to introduction of the explosive into a process. This data and recommendations of the committee must be available to the processing group prior to beginning work.

Compatibility of different explosives should be established before combining them as part of a design, for storage, or for scrap disposal.

Having more than one explosive in a processing building or bay at the same time must be carefully considered for hazards and done only for good reason.

General operating guidelines should be written for all new operations to ensure that careful thought and careful review have been exercised prior to the start of potentially hazardous work. The general operating guidelines may permit flexibility where justified, but they must be reviewed by one or more qualified, experienced persons.

Keep up-to-date charts and instructions in the operating building. They can serve as ready references, as reminders of procedures to be followed and explanations of the essential features of equipment.

Time must be allowed - even at the expense of deadlines and schedules - for adequate thought, planning and preparation of hazardous operations.

Within limits of reasonability and practicability, the safest method for processing or working on high-energy materials should be used.

Any explosive operation performed with personnel exposed should be of such a nature that there is no detonation hazard, and with ample opportunity to escape unhurt in case of fire. Usually, operations in closed vessels will be performed remotely.

Responsibilities and Controls

Supervisors are responsible for the safety of operations and the men they supervise. The safety-engineering staff is responsible for advising the line organization on safety and is responsible for helping the line organization to maintain high standards of safety.

Whoever recognizes a hazardous situation is responsible for taking steps to have the condition corrected.

Scrap or waste disposal is a hazardous operation. The scientist or engineer who originates a new formulation is obligated to assist in specifying disposal conditions and procedures.

Most careful consideration must be given to setting processing limits such as maximum temperatures, pressures, rates of machining, rates of mixing, and rates of extrusion.

Containers of explosives and explosive ingredients should be clearly labeled at all times as to their content and nature of hazard. When possible, label the explosive directly.

Explosive-processing or storage areas should be posted with warnings to advise of precautions to be taken and how to obtain guidance.

Minimization of Hazards

The number of individuals exposed to hazards should be kept to a minimum consistent with operational requirements and safety.

Always work with, and in the presence of, the least amount of explosive needed for the operation.

Get as much useful data on as small a scale as possible. It is much easier to protect individuals and minimize losses with laboratory-scale work than with full-scale work.

Check new equipment and new procedures with inert materials whenever possible.

Cleanliness and orderliness help to prevent initiation or the spread of a fire or detonation.

Operations should be conducted at all times with a view toward minimizing the effects of accidental fire, detonation, or any other hazard.

Only the immediately needed portable tools and equipment should be retained in a processing room.

Transportation, Shipping and Storage

With few exceptions, containers should be used for transporting and storing explosives. These containers should provide delay of ignition from fire, should attenuate shock energy, and should protect against contamination and physical damage.

When explosives are transported, precautions must be taken to protect persons and property on or near the roadway. Precautions must be taken to reduce the probability of an accident and to minimize the effects of a possible transportation accident.

Shipping explosives to individuals or activities should be performed by a group or individuals familiar with pertinent regulations governing packaging, shipping, and handling in transit.

Before sending explosives to other activities, it should be established that the activity is qualified to receive and handle the explosive. The receiver should be fully informed in writing of the characteristics of any new or nonstandard explosive.

New or experimental explosives whose stability and compatibility with other materials have not been thoroughly established should be stored in small quantities under conditions where possible ignition will cause limited damage. These explosives must never be stored with large quantities of other explosives.

A periodic review of high-energy materials in storage must be made to ensure against storage of these materials for longer than their safe life.

Facilities and Equipment

The design of new facilities, new equipment, and tools should receive the same careful safety review as do new explosives. Designers should remove the human factor from hazards by making protection as permanent and as automatic as possible.

All automatic safety devices such as fire fighting systems, interlocks, and warning signals should be checked at predetermined intervals or more frequently.

Schedules of preventive maintenance should be set up for all equipment used in explosive operations where failure to institute and conduct such a program can lead to processing hazards.

Equipment taken to a shop for repair or adjustment must be freed from explosives by a suitable decontamination process. Shop personnel should be warned of added precautions to be taken during further disassembly.

All explosives must be removed from a processing room when it is turned over to a maintenance group for repair or adjustment of equipment. Equipment that may be contaminated with explosives must be cleaned so that repairs or adjustments can be made safely. Maintenance personnel should be given complete information on conditions that might affect their safety.

Although every reasonable effort has been made to decontaminate a facility or equipment, anyone performing maintenance or repair work on the equipment should proceed with caution.

Reporting Accidents

The discernible facts associated with any accidental deflagration or explosion must be reported completely and accurately so that others doing similar work may be warned and so that the best corrective action may be taken to prevent similar accidents.

Minor incidents, which in themselves do little or no harm, frequently give warnings of unsuspected hazards. These incidents should be widely reported and their significance given thorough consideration.

Complete records of operating conditions should be kept. When accidents occur, the records are an important aid in determining the cause and in preventing future adverse incidents. Critical temperatures, pressures, speeds, power consumed by motor, etc., should be recorded continuously when possible.

SUPPLEMENT A

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SUPPLEMENT B .. CHECK LIST

The most important objective of this report was stated in the "Introduction" in the following words.

"In summation, these services require all workers with high energy compounds and compositions to learn and understand the experience of all those who have any knowledge of the compound, composition, or process involved."

In order to achieve this objective it is helpful to have a list of sources of information which will ensure that none are missed in the search for information. Such lists were discussed more fully in the Introduction.

1. Objective. The compound or composition to be prepared should be stated here. The scale or scales of operation and amount of material in each batch should also be stated.

2. Properties.

- (a) Heat of formation and source of information.
- (b) Heat of combustion and source of information.
- (c) Free energy of formation.

3. Public abstract literature.

- (a) Chemical Abstracts (since 1906)

Subject indexes, annual and decennial

Formula "

Patent "

4. British Chemical Abstracts (since 1925).

5. Chemisches Zentralblatt (since 1829).

6. Angewandte Chemie.

7. Original publications cited in abstract journals. Record information found in original publications.

SUPPLEMENT B (cont'd)

8. Information found in text books with references to original publications if given.

9. Technical publications such as:

(a) Memorial des Poudres

(b) Zeitschrift fur das gesamte Schiess- und Sprengstoffwesen (1906-1904). (This has been continued under another name, Sprengtechnik (1952)).

10. Extensive collection of classified literature and reports are available at the following:

Naval Ordnance Laboratory (WO)

Picatinny Arsenal

Bureau of Naval Weapons Library

Armed Forces Technical Information Agency (ASTIA)

Solid Propellant Information Agency (SPIA)

OSRD 2014 - Compilation of Data on Organic Explosives.
(Declassified). Available (photocopy or microfilm at Library of Congress).

11. Personal conversations with earlier workers with the materials involved.

The above is not intended to be a complete check list or to be suitable for specific activities. Each activity is advised to make a check list which should be used with imagination. Reference (9) will be helpful in making a check list for literature searches. Some details of all information found should be given and failure to find information in each source explained. Subjects sought in the abstract journals should be listed. Any and all other information should be included. The result of the search must be such that a reliable conclusion about its completeness can be made.

All opinions about compatibilities of ingredients should be included.

SUPPLEMENT C

APPROVAL FOR POTENTIALLY HAZARDOUS OPERATION

CHEMICAL LABORATORIES - Room _____ PILOT PLANT AREA - Bldg. _____

Purpose of Operation: _____

_____Materials To Be Used: _____

_____Expected Range of Conditions: Temp. _____ Pressure _____ Others _____Equipment or Apparatus: _____

_____Operation Procedure: _____

_____Safeguards: _____

_____Location: _____Personnel: _____ Expected Duration of Program: _____Do you consider the proposed program hazardous? _____ If so, in what respect? _____

_____Do you consider the above safeguards adequate? _____Has a literature search been made of the hazards involved? _____If so, list pertinent references. _____Submitted by: _____ Date: _____

Approved as listed above, with attached additional precautions and safeguards.

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